BIOGEOCHEMISTRY of the WORLD'S LAND

DOBROVOLSKY

ADVANCES IN SCIENCES AND TECHNOLOGY

Biogeochemistry of the World's Land

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ADVANCES IN SCIENCE AND TECHNOLOGY

Biogeochemistry of the World's Land

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PREFACE

Humanity's ever growing impact on the environment, and the consequent local and global effects demand a deeper understanding of the mechanisms underlying maintenance of dynamic equilibrium in the biosphere and how it evolves. The concepts and ideas of biogeochemistry that the normal state of biosphere is ensured by a system of cycles involving the mass exchange of chemical elements between living organisms and the environment, appear to be quite productive in this high-priority scientific discipline. In this system, the active principle comes from living organisms whose global geochemical activity alters slowly but inexorably the environment, which, in turn, makes the organic world evolve.

The purpose of this book was to generalize the essential facts and ideas about biogeochemical cycles and the mass distribution of chemical elements in the world's land biosphere. The reason for this endeavour is undoubtedly because the predominant mass of the Earth's living organisms is confined to land. The land is also the habitat of humanity, and it is the land that has had to sustain the onus and odium of humanity's productive activities. The study of biogeochemical processes that occur on land is therefore an important issue.

The land, to a first approximation, is one of the two general blocks of the biosphere (the other is the ocean). For this reason, the overall estimated mass of the elements in biogeochemical cycles on land provides a basis for estimating the material balance on a planetary scale. A more detailed approach show that the rate of biogeochemical processes and the migrating mass is strongly susceptible to hydrothermal conditions on the Earth's surface and several other factors. In view of this, the emphasis is on the features of biogeochemical cycles in the major natural zones and, particularly, at the land-ocean interface where the cyclic mass exchange processes are subject to the enormous power of the ocean.

This book is to a certain extent a summary of the author's experience and experimental biogeochemical material collected in the tundra, taiga, steppes and deserts of Eurasia, in the tropics of Africa and on islands in the Indian and Arctic oceans. The author wishes to express his gratitude to his colleagues and friends who shared with him the romance and labour of these explorations. The author's special appreciation is addressed to the American biogeochemist Dr. H.T. Shacklette for his support for this book and for his invaluable service in editing the English text of the book. It would also never have seen the light of day were the author's endeavours deprived of the constant aid of M.K. Dobrovolskaya, whose lively optimism was a major support to the author in this period of severe trials for Russia.

V.V. Dobrovolsky

INTRODUCTION

Biogeochemistry is an interdisciplinary merger of the 20th century that has taken its origin at the borderline of problems of biology and geochemistry. As its name suggests, biogeochemistry is concerned with the role and influence of biotic activity on geochemistry, that is, with the impact of living organisms on the migration and distribution of chemical elements in the Earth's crust.

1. Basic Concepts

The concept of the living matter and the notions about the biopshere that have been suggested by V.I. Vernadsky constitute the theoretical basis of biogeochemistry.

The concept of the living matter is seen in the following. The living organisms, while differing vastly among themselves in size, morphology, and physiology, share nonetheless a basic feature common to them all: to be able to exist, they must be involved in the metabolism with their habitat. The living organisms are known to account for a negligeably small portion of the mass of the Earth's outer envelopes; nonetheless, the overall effect of their geochemical activity in the metabolic processes extends to a planetary scale. Since the living organisms absorb chemical elements selectively, in accordance with their physiological needs, a biogenic differentiation of elements occurs in the environment. Of no minor importance is also the geochemistry of metabolism. Gaseous metabolites are released into the Earth's atmosphere, thereby making its compostion gradually vary. Liquid metabolites and decay products affect the acid-base and reduction-oxidation processes in native waters which transform the upper lithospheric layers through leaching chemical elements from it; the licheates become involved in the water migration and finally take part in the compositional buildup of the World's ocean and the formation of sedimentary rocks.

An individual organism is perishable, whereas life, sustained by succeeding generations, is perpetual. The action of living organisms on the environment, not interrupted for a shortest moment in the course of the entire geological history, has continued for about 4 thousand million years. Therefore the perpetual planetary totality of organisms may be regarded from a geochemical standpoint as a specific form of material entity, the living matter. Its major property is the incessant and continuous mass exchange between the chemical elements and the surroundings. For this reason, the living matter plays the role of a decisive factor in geochemical evolution of the outer layers of the Earth.

The concept of living matter is an issue that has been attracting a close attention of the experts of both natural science and philosophy. The phenomenon

of living matter harbours much of the obscure and enigmatic. The origin of the living in the living as the only possible evolutionary pathway has not as yet been substantiated scientifically; however, our knowledge of the problem provides a reason to regard Life not only as a terrestrial, but also as a cosmic phenomenon. V.I. Vernadsky (1863-1945), relying upon the works of L. Pasteur (1822-1895) and P. Curie (1859-1906), advanced an idea that the living matter existed in a specific space whose geometry was distinct from the geometry of the space for existence of terrestrial nonbiogenic bodies. In his philosophical world outlook, V.I. Vernadsky was congenial with the prominent French paleontologist and thinker P. Teilhard de Chardin (1881-1955) and shared the latter's idea that "Prise dans sa totalité, la substance vivante répandue sur la Terre dessine, dés les primiers stades de son évolution, les linéaments d'un seul et gigantesque organisme".* Without going into the particulars, we can with confidence affirm that the living matter plays a very important role in the actual chemical composition of the outer shells of our planet.

The concept of biosphere. The term "biosphere" was coined by the Austrian geologist E. Suess (1831-1914) in 1875. He used this term to indicate the outer sphere of the Earth that was inhabited by living organisms. V.I. Vernadsky has advanced the concept of the biosphere as an outer shell of the Earth subject to the geochemical activty of the living matter. An essential point to be emphasized is that the biosphere is currently conceived not merely as a habitat for living communities, but rather as a global system within which inalienably coexistent are, on the one hand, the inert matter in solid, liquid and gas phases, and, on the other hand, the vast variety of diverse forms of life and their metabolites. The biosphere is envisaged therefore as a unity of the living matter and the outer part of the Earth's globe. The living matter is inconceivable without the biosphere as well as the biosphere makes no sense without the living matter.

One will easily have perceived the importance which is attached, within the above conceptual scheme, to the interaction between living matter and inert material of the Earth. This interaction is effected as an exchange of chemical elements between the living organisms and their environments. It is precisely the processes of element exchange that provide an objective characterization for the geochemical activity of organisms, and it is owing to them that the biosphere possesses and maintains a definite "geochemical organization", speaking in the words of V.I. Vernadsky. These processes which are in essence geochemical (as natural migrations of chemical elements) and which are effected not by the action of geological factors, but through the agency of living organisms, have been termed biogeochemical by V.I. Vernadsky. It stands to reason that biogeochemical processes are the subject matter for biogeochemistry.

*"Taken in its entirety, the living matter that has spread on the Earth outlines, from the earliest stages of its evolution, the features of a single and gigantic organism". P. Teilhard de Chardin. Le Phénomène Humain. Editions du Seuil, Paris, 1955, p.119.

Cyclicity of biogeochemical processes. In studying the interaction between the living organisms and their environment, the scientists very soon became aware that the processes of biogenic mass exchange were cyclic in character.

Life is cyclic by nature. The idea of the perpetuation of life through the never-ceasing process of death and reproduction of individual beings in their entire diversity is inherent in the religion and world outlook of all the ethnoses. The famous biblical dictum condemning all the mortals arisen from the ashes to turn again to dust and ashes has become transformed, by dint of the imaginative scientific intellect, into a theory of biogeochemical cycles of chemical elements which are involved in mass exchange and which serve to maintain, in a compositionally equilibrated dynamic state, both the living matter and the major components of environment: atmosphere, soil, land, water and the World's ocean.

The studies carried out during the recent decades have shown that the life cycles of individual organisms and their communities are connected with the cyclic processes arising from geophysical and cosmic events such as the rotation of the Earth about its axis and about the Sun, the natural evolution of solar matter, the displacement of the solar system within the Galaxy, and others. The mass exchange cycles of different extension in space and of various duration in time constitute the dynamic system of biosphere.

The migration of chemical elements being effected not through isolated communication channels but in thermodynamically open systems does by no means lead to chaos. The direction of mass transport is kept under control by a large variety of diverse equilibria. Simultaneously, the system of equilibria provides for a specific feature of the migration cycles of biosphere, viz., their openness, which is of exceptional importance for the functional mechanisms of biosphere.

V.I. Vernadsky was of the opinion that the history of most chemical elements that constitute 99.7% of the biosphere mass could be well explained by the concept of circulatory migrations. He made it a point to emphasize that "... these cycles are reversible only for a larger part of the elements involved, whereas a smaller part of elements are inevitably and continually lost from the circulation. This exit of elements is final, that is, the circulatory process is, strictly speaking, irreversible".* The incomplete reversibility of migratory masses and the imbalance of migration cycles admit of definite limits for the concentrational variation of a migratory element to which the organisms are capable of adapting themselves; simultaneously, this provides for the removal of the excess element from a given cycle.

Biogeochemistry of the World's land. The bulk of living matter is confined to the World's land. The terrestrial biogeochemical processes are very extensive and play an important role in maintaining the entire biosphere in dynamic

*V.I. Vernadsky. Ocherki geokhimii (The Essays on Geochemistry), Georgeonefteizdat, Moscow, 1934, p. 31.

equilibrium. Alongside with this, the land is the habitat for human species and the main area of human productive activity. Exactly for this reason, the most profound deformations of natural cyclic mass exchange processes and even the impairment of separate links of the biosphere take place on land. In the light of the above explanation, the specific problems of World's land biogeochemistry come to the foreground of major concerns confronting mankind.

2. Historical Development of Biogeochemistry

The shaping of biogeochemistry into a self-sustained discipline was a slow process and proceeded largely in parallel with the general development of chemistry. As has been mentioned above, the basic concepts of biogeochemistry are focused on the assessment of life phenomena and the activity of living matter from a scientific standpoint, that is, through making use of "number and measure". Still, the innovative ideas in biogeochemistry could not avoid interference with the domain of traditional interests of religion, philosophy and, consequently, ideology. In all times, these circumstances were laying a high claim to the personal qualities and endowments of the investigator. Undoubtedly, many scientists have contributed through their selfless labour to the development and acceptance of new ideas in biogeochemistry; however, the truth is also that the most spectacular and triumphal achievements in the field were linked to the names of remarkable individuals who excelled not only as eminent scientists, but also as brilliant and exceptional personalities.

The latter part of the 18th century witnessed the discovery of oxygen, nitrogen, and carbon dioxide, which enabled one to establish the composition of atmospheric air. The scientific communities of Paris and London were engaged in heated discussion about the role of gases in plant life. By that time, the distinguished French chemist A.L. Lavoisier (1743-1794), one of the founders of modern chemistry, obtained a solution to the problem of quantitative determination of chemical elements involved in a reaction; he also studied the phenomenon of equivalent exchange of oxygen and carbon dioxide in plants. In those works, he layed a basis for the current ideas of carbon geochemistry in the biosphere. Lavoisier provided evidence that the major chemical element of organic matter, carbon, was supplied to the plants from the air, and subsequently carbon was released into the atmosphere as a constituent of carbon dioxide from the decayed plant remains. These findings brought him to a conclusion about the existence of a universal turnover of elements involved in the interaction of living organisms with nature. Shortly before his execution by the merciless order of a revolutionary tribunal, Lavoisier published a treatise "The Turnover of Elements on the Surface of the Terrestrial Globe" in which

he substantiated the idea of a cyclic exchange of chemical elements among three kingdoms of nature: mineral, vegetable, and animal. In this treatise dating back two hundred years, he posed the question, an answer to which has become the major concern of modern biogeochemistry: "What are the ways the Nature makes use of in performing this amazing turnover of matter among its three kingdoms?".

The concept of Lavoisier on the cycling of chemical elements in nature found later an ardent supporter in the person of G. Cuvier (1769-1832) who, in his famous report to Napoleon Bonaparte (1769-1821) on the development of science in France within a period of 1797 to 1808 defined life as a rapid and intricate vortex entrapping the molecules with definite properties.

The works of Lavoisier brought forward the evident fact that the living organisms were mainly composed of elements that could form gases at the Earth's surface and that the relationship between the organisms and the atmospheric gases was of exceptional importance for the chemistry of life. This problem remained a major concern for the scientific thought in the beginning of the 19th century. In 1841, two prominent French scientists, the famous chemist Jean-Baptiste Dumas (1800-1884), one of the founders of organic chemistry, and his namesake Jean-Baptiste Boussingault (1802-1887), the founder of agrochemistry, a voyager and naturalist, suggested a definitive formulation of the concept of cyclic turnover of gases in the system of living organisms and atmosphere through expressing this concept in a vivid and somewhat paradoxical form: "... We see that the primary atmosphere of the Earth has become divided into three major parts: of these, the first part constitutes the actual atmospheric air, the second part has been conceded to plants, and the third, to animals... Thus, all that the air gives to the plants pass on to the animals, and the animals return it to the air; this is a perpetual circle within which life palpitates and manifests itself and where matter merely changes its place" (Dumas and Boussingault, 1844).*

However, the exchange of matter between the living organisms and the environment is not confined solely to the gas turnover, however great may be its importance in nature. The next step in the understanding of biogeochemical cycles on land was linked to the works of the eminent German chemist Justus Liebig (1803-1873). He showed that the chemical elements were supplied to plants via two routes: some of them from the air (for example, carbon), the others, as aqueous solutes from the soil. Liebig conducted wide-scale studies on soil composition, and the content of mineral materials in various organs of plants and animals and products of their metabolism. In fact, he was the first to apply a method of cross-spectrum analysis currently in wide use by modern geochemistry.

*Translation of a Russian citation in: V.I. Vernadsky. Ocherki geokhimii (The Essays on Geochemistry), Gorgeonefteizdat, Moscow, 1934, p. 172.

Based on vast analytical evidence, Liebig showed that the plants absorbed chemical elements selectively from the soil. He developed his famous theory of the mineral nutrition of plants and layed the grounds for studying the cyclic migration of elements within a soil-plant-soil system, later known under the name of the biological cycle.

The importance of Liebig's works for biogeochemistry is hard to overestimate. Liebig outlined routes to experimental studies of biogeochemical cycles for most chemical elements and transferred the problem of interaction between living organisms and mineral nature from the realm of philosophical speculations onto the solid basis of scientific research and practical activity. Owing to his works, the biological cycle of chemical elements shaped itself into a tangible reality. Liebig showed the possibility of human control over this process through judicious introduction of additional amounts of elements into the migration cycles. In his well-known book *Organic Chemistry in Its Application to Agriculture* which saw the light in 1840 in Germany, a pioneering attempt was made to predict the effect arising from a disturbed natural mass exchange of certain chemical elements on the fate of peoples and stages. Even the present day reader cannot remain indifferent to the analytical perspicacity, extensive knowledge and scientific applicability of Liebig's works.

At the turn of the 19th and 20th centuries, the seemingly inviolable frontiers between the traditional natural sciences showed a tendency to give way to new interdisciplinary mergers. The appearance of such borderline, "synthetic" disciplines has provided the impetus for wider scientific research and finally enabled more detailed studies both of separate components of nature and the interactions arising between them. The genetic pedology or, less academically, genetic soil science that has arisen in the 1880s in Russia was in fact a precursor to the said tendency.

The founder of this new branch of knowledge was the prominent Russian scientist V.V. Dokuchaev (1846-1903), then a professor at the Saint Petersburg University. Dokuchaev regarded the soil genesis as a result of interaction of many soil-forming factors, viz., soil-forming rock, biological activity of plants and animals, climatic conditions, surface relief, ground waters, and others. The soil is made up of diverse components, both living and nonliving, which makes it different from simpler natural bodies, for example, any rock composed only of minerals. The living edaphic organisms make up an inalienable part of the soil, as well as do the mineral particles.

The soil, deprived artificially of the edaphic organisms, is doomed to perish. Plants, animals, mesofauna, and microorganisms are involved in intricate interactions both among themselves and with the mineral matter, metabolites and decay products, and thus form the soil and maintain its dynamic existence. The interaction of living edaphic organisms with inorganic soil components is, in turn, intimately related to the climatic, relief, and hydrologic conditions,

and, for this reason, different geographical zones and different landscapes develop distinct types of soil.

The theory of Dokuchaev provided clues to a deeper insight into the biological activity of living organisms inhabiting an extensive geological formation, the soil cover of the World's land. Simultaneously, the living organisms were shown to constitute an indissoluble unity with other parts of the ecological system whose very existence is unthinkable without biotic phenomena.

The ideas of V.V. Dokuchaev received little understanding among his contemporaries but, luckily, were not lost on his disciples who contributed significantly to many related branches of natural science.

These were, to briefly summarize, the bench-marks in the ascention of scientific thought about the planetary involvement of living organisms and their close relationship to the nonliving environmental matter. Abundant, but disparate and seemingly incompatible facts and hypotheses required their generalization on a new methodological basis. This basis has been furnished by geochemistry, a branch of chemistry that focuses its attention not on the chemical species occurring in nature, but rather on their constitutive elements and proportions thereof.

As stated by the principles of geochemistry, any material object can be characterized by the proportion of its constituent chemical elements. The geochemical approach permits us to compare and correlate diverse natural bodies and processes. In particular, given the knowledge of an average overall composition of Earth's living organisms and an average composition of Earth's crust, one may attempt to assess the temporal characteristic of geochemical biotic activity. Also, having determined the annual uptake of chemical elements by the World's land vegetation and comparing it to the annual global stream loss of the same elements, one can form an idea of the relationship of these two planetary processes. Thus, the geochemical approach provides for an objective, scientifically-based assessment of the biotic activity, both in toto and of separate biotas.

Geochemistry, whose emergence has been predetermined by the general progress of earth sciences took, nonetheless, different routes for its development in different countries. In the USA, the initial priority was given to a statistical study of chemical element distribution. In the 1880s, F.W. Clark, a chemist at the United State Geological Survey (USGS), set for himself a goal to determine the mean concentration for ten major chemical elements in main rock types, natural waters and other media on the basis of available analytical data. Within a period of 1889 to 1924, he published a number of reports containing replenished and updated results for mean contents of chemical elements. His book *The Data of Geochemistry* was the first substantially documented evidence for distribution of major chemical elements over the Earth's crust.

In Europe, geochemistry was shaping on the basis of mineralogy, a science concerned with naturally occurring chemical compounds and their formation. For this reason, the attention of European geochemists was turned to the processes responsible for chemical element distributions.

In Norway, the Oslo University could take credit for a traditionally strong school of mineralogists and chemists whose major interests were concerned with the distribution and proportion of elements in physicochemical processes of ore and rock formation. The eminent geochemist V.M. Goldschmidt (1888-1947) was a disciple of that school. In the 1930s, he advanced a theory of the global distribution of chemical elements depending on their atomic structure. The basic principles of his theory were expounded in his famous report to the Chemical Society of London in 1937 (Goldschmidt 1937).

In Russia, mineralogy was established under the auspices of the Moscow University, at the Chair of Mineralogy. V.I. Vernadsky, the then head of the Chair, lectured on an original course of genetic mineralogy. In his teaching program, the major emphasis was put on the dynamics of mineral formation, rather than on the outward properties and attributes of minerals, an approach typical of the classical descriptive mineralogy. In studying problems in the history of minerals, V.I. Vernadsky eventually came to the idea that the natural processes of mineral formation should be studied at an atomic level. Subsequently, he advanced the basic principles of geochemistry concerned with the migration of chemical elements, the role of isomorphism in the distribution of elements over the Earth's crust, the forms of occurrence of elements and their dispersal.

These principles have to a considerable extent highlighted the routes which biogeochemistry took in its further development. V.I. Vernadsky belonged to a pleiad of eminent scientists and thinkers of the 20th century. His versatile activity could not pass unnoticed in the history of science. He was the founder of a number of novel scientific disciplines, biogeochemistry included. The culmination of his scientific creativity was a theory of living matter which was focused on the role of biotic processes in planetary geochemistry and on the biosphere, a unique envelope generated by living matter within which the Earth is enclosed.

The starting scientific and philosophical basis for the Vernadsky's concepts of genetic mineralogy, geochemistry and, later, biogeochemistry and biosphere were the Dokuchaev's ideas that all the components of nature were closely interrelated and that the living organisms were an inalienable integral part of the soil and simultaneously its essential formative factor.

In 1916, V.I. Vernadsky set about constructing a "science of life", to which he devoted many years of hard labour. It was necessary, for one thing, to work out a methodology that would enable an objective scientific assessment of both the living matter and effects arising from its activity. The routes to a solution of this entirely new problem were outlined by Vernadsky in 1918-1919 when

he organized, for the first time, biogeochemical studies in the Ukraine, in his capacity as the President of the recently instituted Ukrainean Academy of Sciences. In the early 1920s, he expounded his ideas in reports to the scientific communities of Petrograd and Prague and later in a course of lectures delivered at the Sorbonne University.

V.I. Vernadsky believed that "... in order to be able to correctly assess the geochemical role of living matter and to express it in quantitative terms, we must know, firstly, the mean elemental chemical composition of all the organisms of living matter and, secondly, we must know the weight of living matter. This composition and this weight must be correlated to the weight and composition of the medium ... within which the terrestrial matter is found".*

Owing much to the persistence of V.I. Vernadsky, the Biogeochemical Laboratory at the Academy of Sciences, USSR, was instituted in 1928; he was its head till the last days of his life. Regrettably, no large-scale experimental studies on the distribution of chemical elements in various organisms could be carried out at that time because of the limited personnel of the laboratory and scarcity of material means. The large and laborious research program in quantitative determination of living organisms could not therefore be implemented. However, later in the second half of the 20th century, this program has received a new impetus owing to the efforts of numerous ecologists, soil scientists and oceanologists.

3. Biogeochemistry Related to Geochemistry and Biology

Methodologically, biogeochemistry is closely related to geochemistry. These two disciplines are concerned with the distribution of chemical elements in space and in time, with the origin and transformation of elements of different occurrence, their migration, dispersal and accumulation under different natural conditions. The distinction between the two is that geochemistry explores mainly the behaviour of elements in natural solutions, melts and crystallization products whose state and transitions are governed by the laws of thermodynamics, physical chemistry and crystal chemistry, whereas biogeochemistry studies the migration and distribution of chemical elements in biosphere where the main motive force is biotic activity of organisms. This distinction bears a close similarity to the distinction between inorganic and biological chemistry. Unquestionably, there may arise natural conditions and processes in which the laws of geochemistry cannot be divorced from the laws

*V.I. Vemadsky. The Chemical Composition of Living Matter as Related to the Earth's Crust Chemistry in: Biogeokhimicheskie ocherki (Biogeochemical Essays). AN SSSR, Moscow-Leningrad, 1940, p.12.

of biogeochemistry. The ideas of V.I. Vernadsky as to the planetary role of living matter have largely contributed to the theory of geochemistry and provided a clue to the understanding of essential geological processes, in particular, sedimentary ore formation.

Biogeochemistry is also closely related to other earth sciences, notably those concerned with the composition of rocks, minerals, natural waters and gases and with the environmental development in the course of geological history.

The response of the experts of biological sciences to Vernadsky's ideas was not devoid of scepticism and ambiguity. Vernadsky affirmed that studying a living organism apart from its natural milieu meant committing a gross methodological error since the two entities were indissolubly linked to each other. "Biologists, in their studies of living organisms, mostly leave unheeded the indissoluble ties, the exquisitely intricate functional dependence that exist between the living organism and its environment ... complex natural phenomena are replaced by oversimplified models".*

Simultaneously, biogeochemistry was critically viewed by the representatives of physicochemical biology who found no practical reason in determining the content of a chemical element in an organism without understanding its involvement in concrete organic compounds, deciphering their molecular structure and specifying the type of bonds linking the given element to others. A remark on this point is that the major task the biogeochemical study is concerned with is the exchange of chemical elements between the living organism and the environment.

This task is not a priority in the sphere of interest of disciplines affiliated with the physicochemical biology (biochemistry, bioorganic chemistry), but is congeneric to the aims pursued by biological sciences whose primary concern is the study of the ties between organisms and their habitat: geobotany, biocenology and, especially, ecology. In studying ecosystems, a great emphasis is put on the mass exchange in them.

The geochemical effects arising from the activity of microorganisms with their very rapid life cycle argue convincingly for a pivotal statement of biogeochemistry: the compositions of living organisms and their environment are intimately interdependent. For this reason, the principles of biogeochemistry have gained a welcome acceptance by microbiologists. On the one hand, the microbiologists established that the chemical composition of water confined to a closed basin tends to vary by the biological activity of microorganisms; these, also, play an important part in the global gas regime. On the other hand, the limicolous and humicolous organisms (bacteria and actinomyces) can adapt themselves to widely ranging concentrations of cobalt, molybdenum, copper, vanadium, uranium, selenium, and boron. This adaptability is hereditary, and

*V.I. Vernadsky. Ocherki geokhimii (loc. cit.), p. 38.

for this reason, the adaptation of microorganisms is effected through a rearrangement of their populations.

In the USSR, the principles of biogeochemistry have advantageously been applied to soil science and landscape science. The well-reputed soil scientist, geochemist and geographer B.B. Polynov (1877-1952) has developed, on the basis of the Vernadsky's concepts, a theory of landscape geochemistry. Further progress in biogeochemistry was accomplished owing to the works of Polynov's followers, geochemical soil scientists and geochemical landscape scientists. Currently, one would hesitate to draw a clear bordering line between the fields concerned with biogeochemical, ecologogeochemical, soil-geochemical and landscape-geochemical studies.

4. Practical Applications of Biogeochemistry

By virtue of the fact that the major spheres of productive activity of man (agriculture and industry) are confined to the land, the routes to practical use of biogeochemistry also bear relevance to the processes occurring on the World's land. Until recently, the most effective practical application of biogeochemistry has been associated with geological survey or, more precisely, with the so-called biogeochemical method of prospecting for minerals.

In essence, this method consists in identifying floristic areas where plants and their vegetable remains and metabolites reveal elevated concentrations of ore-forming elements.

The areas of elevated metal concentration in plants and in the top soil horizon are biogeochemical anomalies and are thus suggestive of the eventual occurrence of deep ore deposits. If this is the case, the biogeochemical anomalies may be regarded as dispersion halos of ore accumulation. They are formed via involvement of metals in the biologic cycle and their accumulation in plants and in the soil. The biogeochemical method facilitates and makes less costly the mineral prospecting in forest regions difficult of access or in areas of detrital allochthonous deposits.

The analysis of metal in plants as a method for ore prospecting started to find application in the mid-1930s in the USSR, Norway, Sweden and Finland. N.J. Brundin initiated his experimental studies in Sweden and in Cornwall, the ore-bearing region of long standing in England, and took out, in 1939, a patent for ore deposit prospecting by the chemical analysis of metals in vegetation. Starting from the 1950s, this method has gained a wide acceptance in the USSR, Canada, tropical Africa, Australia, New Zeland, Indonesia, Sri Lanka, New Guinea, and New Caledonia. The applications of the biogeochemical method were reviewed by Malyuga (1963), Kovalevsky (1984), Brooks (1983), and others.

Biogeochemical studies have proved to be very helpful in the discovery of numerous deposits of nonferrous and rare metal ores, uranium ores for the atomic industry and other minerals. At present, the biogeochemical method is known in its several updated versions that have been designed on the basis of recent progress in biogeochemistry and modern instrumentation.

A second practically important trend in biogeochemistry is the study of the effects of environmental levels of chemical elements on human and animal organism. We wish to emphasize that the case in point is the concentration of chemical elements specified by the natural factors only. In certain regions, the geochemical departures, much above the normal level, were known to elicit responsive, occasionally pathologic reactions in living organisms. Such regions have been named biogeochemical provinces (Vinogradov 1962).

In the USSR, Koval'sky and coworkers (1974) have shown that the productivity in cattle can be correlated to the excess or deficiency of boron, cobalt, copper, molybdenum and selenium in animal feed. Similar studies were carried out in England and Ireland by J. Webb (Webb 1964; Webb *et al.* 1966) and in the USA, by R. Ebens (Ebens *et al.* 1973).

As has been reported, the level of microelements in drinking water and foodstuffs of local production can affect human health. The Canadian biogeochemist Warren (1961) was one of the first to attract attention to that problem. Along with the well-known cases of thyroid gland malfunction caused by iodine deficiency, it is of interest to mention a study by Shacklette (1970) relating the level of microelements in soil and plants to the incidence of cardiovascular diseases in the State of Georgia, USA. The Finnish geochemist Salmi (1963) reported a relationship between the concentration of lead in rocks and the incidence of multiple sclerosis. In the USSR, a technique for mapping natural geochemical conditions has been worked out for hygienic and prophylactic management (Dobrovolsky 1967).

In the latter part of the 20th century, the practical needs of agriculture and medicine have stimulated a wide-scale study of trace elements in the USSR. Since 1950, all-union conferences on trace element problems were held each four years in the USSR. The first conference was in Moscow in 1950, and then in Baku (1954), Riga (1958), Kiev (1962), Ulan-Ude (1966), Leningrad (1970), again in Riga (1975), Ivano-Frankovsk (1978), Kishinev (1981), Cheboksary (1986) and Samarkand (1990). Biogeochemists were active participants at those conferences. The information on results of biogeochemical studies of minor elements is regularly reviewed in annually published volumes *Mikroelementy v SSSR* (Trace Elements in the USSR) (1986; 1987; 1988; 1990; 1991). The greatest progress has been achieved in studying trace elements in the soil-plant system. Under the guidance of V.A. Kovda and N.G. Zyrin, the soils of the European Part of the USSR have been mapped for contents of boron, manganese, zinc, copper and molybdenum (*Mikroelementy v pochvakh*

Sovetskogo Soyuza 1973). The two above trends are known in biogeochemistry a long time and have become, in a sense, traditional.

A third trend was gradually forming within a period of the late 1960s and early 1970s and has finally shaped into its official status after the Stockholm Conference which was convened in 1972 under the UNO auspices and was concerned with the preservation and protection of the environment. The world community was showing a growing concern over the productive activity reaching a dangerous level detrimental to the natural conditions.

Efforts were made to coordinate studies on the content and distribution of hazardous pollutants and to work out national and international programs for the control of environmental pollution and for the preservation of normal conditions in the the biosphere. The actually accepted UNO environmental programs are: United Nation Environment Program (UNEP), Global Environmental Monitoring System (GEMS), Man and Biosphere (MAB) and, especially, the Global Changes Program. The programs are supervised by the UNESCO and the Scientific Committee on Problems of the Environment (SCOPE).

Biogeochemistry, primarily concerned with the migration and mass exchange of chemical elements can serve as a theoretical basis for comprehensive biospheric studies in the implementation of the above-mentioned programs. It appears therefore quite natural that the biogeochemists have taken an active part in the study of the actual geochemical state of natural systems of the World's land and their transformations as caused by the poductive activity of man. In particular, in the USA, a national-scale work has been carried out, under the guidance of H. Shacklette, the senior biogeochemist at the United States Geological Survey, on the study of chemical element distribution in soil-forming rocks, soil, and vegetation; in separate regions, food products have been analyzed for potential pollutants, and attempts were made to assess the effect of technogenic concentration of certain elements on humans and living organisms (Shaklette *et al.* 1970, 1971, 1974, 1984; Ebens *et al.* 1982; Connor *et al.* 1975). In the USSR, progress has been achieved in the study of biogeochemical cycles of nitrogen (Bashkin 1986), other main elements (*Biogeokhimicheskie tsikly v biosfere* 1976) and heavy metals (Dobrovolsky 1982). A point in fact is that the ecologists, concerned with problems in energy and mass exchange, have arrived, in an independent way, at many of the biogeochemical concepts (Chapman 1976). In the implementation of international programs on vegetation ecology, the biogeochemical cycles of chemical elements in various forest ecosystems have been studied (*Ecology of an Oak Forest in Hungary* 1985; Rapp 1973). The careful quantification of phytomass dynamics sets a particular value upon these researches. It is hoped that from the above brief overview, the reader will have formed an impression of the importance, both from theoretical and practical standpoints, that should be attached to the problems facing the biogeochemistry of the World's land.

1 Terrestrial Living Matter: Composition and Biogeochemical Dynamics

The students of natural sciences of all succeeding ages have made numerous attempts, from all imaginable variety of standpoints, to define and understand life as a global and, likely, cosmic phenomenon. V.I. Vernadsky has formulated, at the beginning of the 20th century, a concept of living matter as a totality of living organisms represented in terms of mass and chemical composition. This concept has provided the theoretical basis for a systematic study of the chemical composition of living organisms and the uptake of chemical elements by living matter. Furthermore, this approach has opened a possibility of comparing the compositions of living matter and inanimate natural formations such as the Earth's crust, atmosphere, rocks, native waters, and others.

1.1. Composition of Living Matter

It had become clear by the end of the 18th century that living organisms are composed mainly of water and gases. In the middle of the 19th century, Dumas and Boussingault arrived at a conclusion that the living organisms constituted a specific part of the Earth's atmosphere. Indeed, both the individual organism and the global living matter contain four major constituent elements capable of forming gaseous compounds at the Earth's surface: oxygen, carbon, hydrogen, and nitrogen.

The compositional determination of any organism, and especially the estimation of the mean composition of the global living matter represents a very complicated and laborious task for many reasons. For one thing, it should be kept in mind that the concentration of the major components of living organisms, water, varies within a very wide range. For example, in plankton the weakly bound water accounts for over 99%, and in the tree trunk, for about 60%. With a view to exclude the effect of variable water content and to reduce the data on chemical element contents to an expression permitting of an easier comparison, the common practice is to calculate the element content by dry weight using an absolutely dry organic material, that is, dessicated to a constant

mass at +102 to +105°C. It stands to reason that in this case we obtain the elemental content not for a real living organism, but rather for its organic matter prepared under specified conditions.

In the dehydrated organic matter dried to a constant weight, carbon accounts for slightly below 50% of the total mass; other major components are oxygen, hydrogen, and nitrogen. The primary organic matter of the Earth's bios is chiefly formed by photosynthesis from carbon dioxide and water; to be noted, water molecules in this process undergo splitting. The hydrogen atoms become incorporated into the structure of organic matter, whereas oxygen is released as a metabolite. If the dry organic matter from a dehydrated organism is subjected to thorough burning, the four major elements are eliminated and the ash remains, which is the sum total of the so-called mineral compounds constituting the organism. An analysis of the ash allows one to determine the proportion of the remaining chemical elements (several tens in number) which make part of the organs and tissues of the living organism. Furthermore, a knowledge of the relative content (concentration) of chemical elements in the ash is essential for comparing with the element concentrations of the mineral substrate on which the organism has grown and which has supplied the ash elements.

It is clear from the above that three variants may be envisioned for expressing the chemical composition of any biological object and global living matter. The relative content of chemical elements can be expressed, first, on a live ("wet") weight basis, second, on a dry weight basis and, third, on an ash weight basis for the organisms in question. Each of these three variants is used for handling specific kinds of problems.

The determination of the abundance of chemical elements in the living matter is also made difficult by the wide variation in concentration of elements in individual organisms. The concentration of elements is dependent on the site of residence, habitat, and developmental stage of the organism. Even in an individual organism, the concentration of the same element in various tissues and organs is subject to variation.

Specifically, the masses of different groups of organisms differ among themselves to a greater extent than the concentrations of elements in various organisms. An account of this circumstance is quite important since the abundance of an element in the living matter of the World's land is estimated by the element concentration in organisms which constitute a predominant part of the mass of living matter rather than by the element concentration in all organisms.

At present, it is a known fact that the higher plants account for a larger part of the mass of living matter of the World's land and entire planet. The mass of living matter of the World's ocean is about 100 times smaller. The mass of terrestrial animals accounts for about 1% of the phytomass. For this

reason the composition of terrestrial vegetation determines the composition of living matter of the World's land and biosphere *in toto*.

In view of the predominance of higher plants, it has been estimated that water accounts for 60%, organic matter for 38%, and ash elements for 2% of the live (wet) biomass of the World's land (Romashkevich 1988). We obtain, on a dry-weight basis, 95% for organic matter and 5% for ash elements.

Data on the average composition of terrestrial organic matter are summarized in Table 1.1. They indicate that the proportion of chemical elements is strongly influenced by the predominance of carbohydrates and lignin. Presumably, carbohydrates account for slightly over 60%, lignin for about 30%, and lipids and proteins for about 5% in the organic matter of the continental phytomass.

Listed in Table 1.2 are the results for relative contents of major chemical elements of the terrestrial phytomass as borrowed from different sources. For comparison, are also given similar results (perhaps, to a lesser degree of reliability) for zoomass. Despite certain appreciable differences, the data on phytomass composition by Bowen and Romankevich may be taken as a basis for estimating the abundance of elements in the living matter of the World's land and the Earth.

To conclude the discussion of major features of chemical composition of the Earth's living matter, one cannot omit mentioning the following. Admitting the uniqueness of the living matter as a phenomenon of our planet, there are known facts suggestive of the connections between the living matter and the Cosmos. This manifests itself in both the structural organization (occurrence of dyssymmetry) and the composition. In analyzing the relative abundance of chemical elements in microorganisms on the one hand and in the interstellar gas and the gas matter of comets on the other hand, Delsemm (1981) has found a remarkable similarity between the two. Our results have shown that such a similarity is also observed for the living matter of the World's land (see Table 1.3). Unquestionably, the elemental abundance must be estimated on the basis of a real live ("wet") biomass rather on a dry-weight basis of organic matter. As starting data for our estimations, we have made use of the results reported by Vinogradov for the wet mass of living matter (see Table 1.2). The abundance of an element has been expressed as the number of its atoms per 1000 atoms of Si.

The relative content of chemical elements gives no idea as to the amount of elements contained in the terrestrial living matter. To know this, one must determine the mass of living matter which will enable one to estimate the mass of separate elements. As has been pointed out earlier, the predominant part of terrestrial living matter is accounted for by plants, notably higher ones.

According to the data reported by Bazilevich and Rodina (1967, 1974) and by Dobrodeyeva and Suetova (1976), the native continental phytomass not affected by the productive activity of man was $6.25 \cdot 10^{12}$ tons, or, on a 40%

Table 1.1. Average Composition of Terrestrial Organic Matter

Biomass and its major components	Chemical elements, %			
	C	H	O	N
Terrestrial plants (Vinogradov 1967)	54	6	37	2.8
Terrestrial biomass (Romankevich 1988)	48	7	41	2
Carbohydrates	40	7	50	1.5
Lignin	62	6	30	1
Lipids	70	10	18	0.5
Proteins	50	7	23	16

dry-weight basis $2.5 \cdot 10^{12}$ tons. Given the average ash content 5%, this mass contained 0.125 ton of ash elements. At present, owing to the productive activity of man, the phytomass has reduced by 25% at least, which amounts to about $1.88\,10^{12}$ tons of which the ash elements account for $94 \cdot 10^{9}$ tons, carbon for $865\,10^{9}$ tons and nitrogen for $36 \cdot 10^{9}$ tons. The masses of other elements as estimated by Romankevich (1988) are (in $1 \cdot 10^{9}$ tons): sulfur, 9; phosphorus, 3.8; calcium, 28.2; potassium, 20.7; magnesium, 6.0; sodium, 2.3; chlorine, 3.8; silicon, 5.6; aluminium, 0.6; iron, 0.5.

The composition of terrestrial biomass is not confined solely to the major elements. One will easily see, on examining Table 1.2, that the compositions of living matter as estimated by different authors share a common feature: the sum of relative element contents very slightly falls short of 100%. The missing part is accounted for by 70 chemical elements dispersed in living matter. They are present in negligible amount and are expressed in μg/g of dry weight or in ppm (parts per million).

The idea of Vernadsky that the living matter harbours all chemical elements met initially with disbelief. The main reason for that long-standing scepticism was that the analytical techniques of that time were not sensitive enough to detect the vanishingly small presence of many elements. A systematic study of dispersed elements in living organisms was undertaken on the initiative of Vernadsky. Vinogradov (1937) was the fist to estimate the average content of chemical elements in the overall mass of living organisms. In the same year, similar estimations were made by Webb and Fearon (1937). It has been mentioned earlier that the relative content (concentration) of major elements in different biological objects or, more commonly, biological sample types is prone to variation. By comparison, the concentrational variation for dispersed

Table 1.2. Relative Content of Major Chemical Elements in Living Matter of the World's Land

Chemical elements	Elemental content in plants, %				in animals, %			
	wet mass (Vinogradov 1954)	dry weight basis	dry matter (Bowen 1966)	ash weight basis	dry matter (Romankevich 1988)	ash weight basis	dry matter (Bowen 1966)	dry matter (Romankevich 1988)
C	18.0	45.0	45.4	—	46.3	—	46.5	51.0
O	70.0	45.4	41.0	—	39.6	—	18.6	26.8
H	10.5	5.75	5.5	—	6.7	—	7.0	7.4
N	0.3	0.75	3.0	—	1.9	—	10.0	9.8
S	0.05	0.13	0.34	6.8	0.48	11.2	0.5	0.5
P	0.06	0.175	0.23	4.6	0.20	4.7	1.70-4.40	1.70-4.40*
Ca	0.50	1.25	1.80	36.0	1.50	35.1	0.02-8.5	0.02-8.5*
K	0.30	0.75	1.40	28.0	1.10	25.7	0.74	0.74*
Mg	0.04	0.10	0.32	6.4	0.32	7.5	0.10	0.10*
Na	0.02	0.05	0.12	2.4	0.12	2.8	0.40	0.40*
Cl	0.02	0.05	0.20	4.0	0.20	4.7	0.28	0.28*
Si	0.20	0.50	0.50	10.0	0.30	7.0	0.012-0.6	0.012-0.6*
Al	0.005	0.013	0.05	1.0	0.03	0.7	0.004-0.01	0.004-0.01*
Fe	0.01	0.025	0.014	0.3	0.02	0.5	0.016	0.016*
Total:	99.70	99.84	99.87	99.5	98.77	99.9		

Table 1.3. Abundance of Major Chemical Elements Constituting Living Matter in Different Media

Chemical element	Abundance, atomic %		
	in cosmos *in toto* (Cameron 1973)	in gas fraction of comets (Delsemme 1981)	in living matter of Earth
H	76.5	56	63.3
O	0.82	31	26.6
C	0.34	10	8.9
N	0.12	2.7	1.2
S	0.0015	0.3	0.01

elements is much larger. The iodine content in sea algae is several hundred times higher above that in terrestrial plants. In ants of the genus *Gamponitinae*, the manganese concentration amounts to several hundredths of a percent, whereas in ants of another kind (genus *Ponerinae*) it is lower by a factor of 1000 (Vinogradov 1963).

The concentration of dispersed elements in organisms of the same species may vary even within the confines of their residence area. For example, the average content of lithium in the vegetation species native to the basin of the Zeravshan River (Central Asia) is varied 100-fold.

Considering that the phytomass composition determines the abundance of elements in the whole living matter of the World's land, of special interest are data on the contents of dispersed elements in plants. At the present time, the pertinent information is well-documented, but it is mostly available for the vegetative organs, whereas other parts of plants were less studied. At the current level of our knowledge, the following estimates for dispersed elements occurring in the vegetation of the World's land may be proposed:

Groups of elements		Mass, million tons
I	Mn	$100n$
II	Sr, Zn, Ti, B, Ba, Cu	$10n$
III	Br, F, Rb, Pb, Ni, Cr, V, Li, Zr	n
IV	La, Y, Co, Mo, J, Sn, As, Be	$0.1n$
V	Se, Ga, Ag, U, Hg, Sb, Cd	$0.01n$

It is to be inferred therefore that the masses of dispersed elements contained in the terrestrial vegetation are quite significant ranging from ten million tons

to ten thousand tons, whereas the mass of manganese approximates the mass of such elements as aluminium and iron.

1.2. Minor, or Trace, Elements

As follows from the above, all of the dispersed elements occur in the living matter of the World's land. They differ in their biological role. Some of them play a definite, occasionally very important part in the vital activity of organisms; the involvement of others remains as yet a controversial issue. Webb and Fearon (1937), on the basis of their analysis of available data on the composition of the Earth's biomass, singled out groups of major and minor nutritional components. Included in the latter were some of the dispersed elements, whose important physiological role had already been ascertained by that time: copper, zinc, manganese, boron, molybdenum, cobalt. Simultaneously, a large number of minor elements of variable occurrence were identified in the living organisms; however, the role of those elements remained obscure. For the first time, an idea was conceived of the qualitatively dissimilar state of major and minor elements in the living matter.

Koval'sky (1974), in summarizing the results of his systematic studies, has divided all the dispersed elements occurring in the mammalians into two groups. Assigned by him to the first group were zinc, copper, iodine, manganese, vanadium, molybdenum, cobalt, and selenium whose essentiality for the organism had been established. Most dispersed elements belong to the second group. They are also of permanent occurrence in animals, but the forms in which they are found have not as yet been sufficiently studied, and their physiological role is poorly understood. There have also been identified elements whose contents are difficult to quantify: scandium, niobium, tantalum, the rare-earth element group, tungsten, and others.

It is noteworthy, that the physiological importance of a trace element is irrelevant to its concentration. For example, cobalt occurring at a level of $n \cdot 10^{-5}$-10^{-6}% (dry weight) is physiologically more important as compared to strontium with its content greater by a factor of 1000.

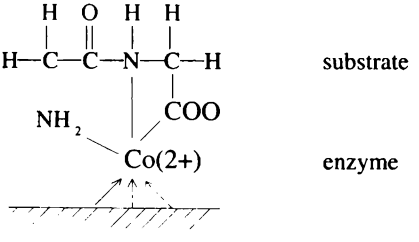
One may venture an analogy between the presence of trace elements in living matter and in crystalline solids. In the crystal lattice, part of these elements are found in a disordered state, whereas the other part become accommodated to the crystal chemical structures, in conformity with the laws of isomorphism. In living organisms, some trace elements are also variable in concentration, whereas others make part of compounds that play a very important role. These compounds, although present in small amounts, provide for the functioning of and control over vital biochemical processes. By way

of example, one may refer to enzymes, hormones, vitamins and their congeners acting as catalysts for such processes.

Enzymes are highly-specialized protein molecules. They take part in important biochemical processes such as photosynthesis, respiration, protein synthesis, hematopoiesis, protein, carbohydrate, and fat metabolisms and others. Many enzymes acquire activating properties through adding a nonprotein group to their protein moiety. Minor elements (most commonly, multivalent metals) or complex organic compounds (coenzymes) can serve for such nonprotein groups. At present, a large number of metalloenzymes are known. Among those are: zinc-containing (carboanhydrase, alcohol dehydrogenase); manganese-containing (arginase, phosphotransferases); copper-containing (tyrosinase, cytochrome oxidase); iron-containing (peroxidase, catalase) and others.

The presence of a minor element ion complexed to the nonprotein group of an enzyme confers a remarkably intensive activity upon these biocatalysts. For example, one molecule of carboanhydrase facilitates, within a period of one minute, the conversion of 36 million molecules of the substrate subject to the action of this enzyme (Lehninger 1974). Interestingly, neither the protein moiety of an enzyme, nor the prosthetic metal taken singly exhibit a high activation energy.

The functions of minor elements in biochemical processes are versatile. The multivalent metals that make part of enzymes play an important role. These metals, owing to their ability to change the state of oxidation, perform the function of electron carriers and participate in the regulation of a number of



important processes such as respiration and photosynthesis. Minor elements provide for the interaction of the enzyme with a substrate. For example, in glycyl-glycine dipeptidase acting on a peptide, the cobalt ion plays the role of a chelating link:

The above example is demonstrative of a case when the activator element forms a tight bond with the protein moiety of enzyme. In such a contingency, the replacement of the element by another one, even congeneric in properties, is difficult, if at all possible, to accomplish. Such a bond is encountered in

enzymes currently referred to as metalloenzymes. Still, in certain enzymes, the minor element may be substituted by another one capable of forming a more stable complex. Minor elements can also form transient unstable complexes with enzymes. In this case, they can be exchanged for congeneric minor elements. For example, in the yeast phosphatase, the function of an activator element can in equal measure be accomplished by manganese, iron, nickel, cobalt and some other metals (Yakushevskaya 1974).

Most commonly, the effects arising from different minor elements are intricately interdependent. The enzymes involved in the cellular respiratory metabolism are activated by copper, zinc, manganese, and cobalt, whereas the oxidation process is stimulated by boron and titanum. Manganese, iron, and copper make part of the enzymes involved in photosynthesis, but the efficiency of this process is influenced by boron, cobalt, molybdenum and some other metals (Koval'sky 1974).

The minor elements play a pivotal role in hormones. The biosynthesis of thyroxin, a human thyroidal hormone, is impossible in the absence of iodine. In health, the amount of iodine in the human thyroid gland is 5-15 mg, and the complete renewal of the available iodine takes 30-50 days. Copper stimulates the activity of pituitary hormones, and zinc, of sex hormones. Minor elements are also indispensable in the synthesis of certain vitamins which are subsequently converted to important coenzymes in the animal organism. Cobalt is a necessary component of vitamin B_{12}, manganese makes part of vitamin C, and zinc and manganese, of vitamin B_1, and so forth.

The uptake and transformation of vegetable matter by animal organisms brings about merely changes in the proportion of minor elements without detriment to their bioactivating role. We wish to refer to the data as reported by Koval'sky (1974). The cobalt-containing vitamin B_{12} becomes converted, in the animal organism, to hydroxycobalamin which is a precursor to coenzyme B_{12}. The latter takes part in the synthesis of amino acids and proteins, ribonucleic acid (RNA), deoxyribonucleic acids (DNA) and other species indispensable for the normal development of organism. Copper is a constituent of many enzymes involved in the metabolism of lipids and chromoproteins, in the synthesis of RNA, DNA, collagen and other species. One should emphasize the functional role of copper in oxidative enzymes. Molybdenum makes part of xanthine oxidase which catalyzes the conversion of xanthine and hypoxanthine to uric acid. Manganese is contained in an enzyme which assists in the development of cartilaginous cells and in osteogenesis. The iodine-containing thyroid hormones control the metabolism and numerous vital functions of the organism.

One will easily have perceived that minor elements are concentrated in the appropriate tissues and organs. As may be presumed, the selective concentration of elements in the living matter of the Earth is a result of the long-lasting

interaction of organisms with the environment. In the course of evolution, the living beings have developed specific biochemical mechanisms in which definite dispersed elements were involved. By virtue of this, the dispersed elements became concentrated in organisms, and the developmental biochemical features became eradicated in succeeding generations and preserved till the present times in the corresponding systematic groups.

The development of biochemical mechanisms and the involvement of dispersed elements in biogenesis is a process highlighted by specific landmarks in its history. There are indications that over 500 million years ago, organisms with hemocyanine blood predominated. In these, the oxygen carriers were biochemically active copper-containing pigments. Organisms with hemoglobin blood evolved later, about 400 million years ago. Probably, the iron-containing hemoglobin provided a better supply of oxygen to tissues. The exit of animals from the sea to the land has necessitated the use of atmospheric oxygen instead of the water-dissolved oxygen.

The evolutionally enforced air respiration was effected through a newly-developed biochemical mechanism in which an active part has been assigned to a zinc-containing enzyme carboanhydrase. The biochemical mechanisms that have evolved at different evolutionary stages of the organic world development are reflected in the specific features of minor element distribution in the living matter.

According to Zavarzin (1984), the primary organisms that thrived 3-3.5 billion years ago in the World's ocean used for building their bodies the energy evolved in oxidation reactions of inorganic compounds, that is, chemosynthesis. In the further course of events, the use of solar energy, that is, photosynthesis, has gained an ever-increasing importance. This process was accompanied by the emergence of a wide variety of complex compounds containing dispersed metals as constituents.

Blue-green algae (*Cyanophyceae*) may be regarded as the most ancient plants. They originated about 3 billion years ago and became widespread within a period of 2-0.5 billion years ago. According to the data of Boichenko (1974), typical of them were high contents of iron, zinc, molybdenum, and chromium. Green algae that emerged 1-0.5 billion years ago developed a higher content of copper in contrast to blue-green algae. The primitive plants on land, as has been established, contained elevated concentrations of zinc and molybdenum.

At subsequent evolutionary stages, the plants started to develop manganese in higher concentration owing to the important role assigned to this element in such crucial biochemical processes as photosynthesis and nitrogen metabolism. The trend in variation of manganese content is very demonstrative. According to Boichenko, the manganese content in heterotrophic bacteria is negligibly small, $n \cdot 10^{-6}$-$n \cdot 10^{-5}$%; in blue-green algae, it is $n \cdot 10^{-4}$%; in green algae, $n \cdot 10^{-3}$%; in filices, $n \cdot 10^{-3}$-10^{-2}%; and in angiosperms, $n \cdot 10^{-2}$-10^{-1}%.

1.3. Biological Cycle of Chemical Elements

Living matter constantly persists in a state of self-renewal. Died-off cells and tissues are replaced by new ones; successive generations of organisms perpetually replace each other. Life is cyclic in its very nature.

The cyclicity of life process is particularly manifest in the dynamics of higher plants which constitute the bulk of living matter of the World's land. The annual death and reproduction of vegetation is accompanied by a cyclic migration of formidable masses of chemical elements.

The most essential aspect of the geochemical activity of plants is the synthesis of organic matter and, as a consequence, redistribution of gases over the Earth's surface. Simultaneously, involved in the migration become a large number of chemical elements from the soil, which are ash remains of burnt plants. The cyclic migration of these "ash" elements in the plant-soil system was discovered by Liebig and is currently known under the name of biological cycle.

The annual growth of natural terrestrial vegetation unperturbed by human activity has been estimated to be $172 \cdot 10^9$ tons of dry organic matter. One may, on the basis of available evidence, estimate the annual amount of elements taken up by terrestrial vegetation. It stands to reason that the average planetary values may differ significantly from the concentrations of elements found in diverse vegetable sample types. The major aim here has been to estimate quantitatively the chemical elements involved in the annual global biological cycle.

The results are summarized in Table 1.4 in two versions: as estimated per overall terrestrial area (excepting areas taken by glaciers, absolute deserts and intracontinental waters) and per square kilometer of this area. The total mass of ash elements involved annually in the biological cycle on land amounts to about 8 billion tons. This value is several times the continental ion stream loss or the overall mass of volcanic ejecta during a period of one year.

The biological cycle of calcium and potassium on land is in excess of one billion tons for each; for silicon, phosphorus, sulfur, magnesium, sodium, and chlorine it amounts to hundreds of million tons per year.

A significant body of published data on elemental contents in plants refers to the deciduous organs: aerial parts of herbaceous plants, young shoots, leaves and needles of trees and shrubs. Because of the lack of standardized procedures in collecting the samples and their preparation for analysis, the wealth of available analytical information is difficult to generalize. For this reason, the average elemental concentrations in the annual growth of continental vegetation should be regarded as preliminary data liable to subsequent correction. Nonetheless, the data listed in Table 1.5 reflect the level of our knowledge

Table 1.4. Uptake of Major Elements and Biological Absorption Coefficient for the World's Land Vegetation

Elements	Concentration in dry phytomass, % (Bowen 1966)	Annual growth uptake		Biological absorption coefficient, K_b
		per overall terrestrial area, $1 \cdot 10^6$ ton/year	per km², ton/year	
N	2.00	3450* (2587)	28.7* (21.5)	—
Ca	1.80	3105 (2329)	25.9 (19.4)	14.4
K	1.40	2415 (1801)	20.1 (15.0)	10.4
Si	0.50	862 (840)	7.2 (7.0)	0.3
S	0.34	586 (440)	4.9 (3.6)	170.0
Mg	0.32	552 (414)	4.6 (3.5)	5.3
P	0.23	397 (297)	3.3 (2.5)	57.5
Cl	0.20	345 (259)	2.9 (2.1)	235.3
Na	0.12	207 (145)	1.7 (1.2)	1.0
Al	0.05	86 (65)	0.7 (0.5)	0.1
Fe	0.02	34 (26)	0.3 (0.2)	0.1

* The parenthetical values are those reduced by 25% to account for productive activity of man.

of the elemental contents in the annual vegetation growth of the World's land and may be used for theoretical estimations and ecological biogeochemical prognosis.

An examination of Table 1.5 will show that the chemical elements are taken up by vegetation not in proportion to their contents in the Earth's crust, but in somewhat different manner. Hutchinson (1943) advanced a suggestion that the accumulation of elements in plants was determined by the ionic potential of elements. The ionic potential defined as the ratio of the charge (oxidation number) of an ion to its radius characterizes the charge density at the ion surface and the degree of hydration of the ion and, consequently, its solubility in water. According to that concept, the elements with low ionic potential capable of forming freely soluble cations, and those with high ionic potential capable of forming freely soluble anions are easily taken up by plants. An in-depth study of the problem has shown that readily soluble compounds can gain, indeed, an easy access to plants, but their retention in the phytomass does not depend in a straightforward manner on the ionic potential. The "geochemical selection" of elements by terrestrial vegetation is determined by a variety of factors. One of the most essential is the ability of an element to build stable complex organic compounds. Alkaline metals are the least apt to this. In plants, they are mostly

Table 1.5. Trace Element Concentrations in Annual Growth of Continental Vegetation

Elements	Average concentration, $1 \cdot 10^{-4}$%		
	in ash	in dry phytomass	in live phytomass
Mn	4100	205.0	82.0
Zn	600	30.0	12.0
Sr	700	35.0	14.0
Ti	650	32.5	13.0
B	500	25.0	10.0
Ba	450	22.5	9.0
Cu	160	8.0	3.2
Zr	150	7.5	3.0
Rb	100	5.0	2.0
Br	80	4.0	1.6
F	70	3.5	1.4
Pb	25	1.25	0.5
Ni	40	2.0	0.8
Cr	35	1.8	0.7
V	30	1.5	0.6
Li	30	1.5	0.6
Co	10	0.5	0.2
La	15	0.8	0.3
Y	15	0.8	0.3
Mo	10	0.5	0.2
I	6	0.3	0.12
Sn	5	0.25	0.10
As	3	0.12	0.06
Cs	3	0.12	0.06
Be	2	0.10	0.04
Se	1	0.05	0.02
Ga	1	0.05	0.02
Cd	0.7	0.035	0.014
Ag	0.6	0.03	0.012
U	0.4	0.02	0.008
Hg	0.25	0.012	0.005
Sb	0.1	0.005	0.002

found as simple ions, their concentrations in the plant cells and in the environmental aqueous solution do not differ appreciably.

By contrast, heavy metals readily build stable complex compounds and can therefore accumulate in the cells. Consequently, the presence of readily soluble ions in the cell sap does not indicate by any means that these ions are concentrated by plants. The selective accumulation of definite elements in plant cells is effected owing to complexness. It is to be understood that these minor elements are accumulated by the cell not in the abstract, but by definite cell components. As has been established, the concentration of chromium in the nucleoproteins of seeds is about 100 times higher over that in the plant cell bulk; accordingly, the concentration of copper in plastocyanin is 800 times, and of cobalt in vitamin B_{12}, tens of thousands of times higher (Boichenko 1974).

1.4. Extent of Biological Uptake

The uptake of dispersed elements by vegetation is a prelude to their involvement in a very specific form of motion, the biological migration. Taking into account the different physiological importance of elements, it may be presumed that the extent of their involvement in this process is also different. A knowledge of the relative content (concentration) of elements in the living matter does not in itself suffice to make a judgement of the extent of their biological uptake. Indeed, one would hesitate to decide which element is better absorbed by vegetation: titanium whose content in dry phytomass is $32.5 \cdot 10^{-4}$%, or molybdenum with its mere $0.5 \cdot 10^{-4}$%?

In order to be able to evaluate the extent of biological uptake of an element, its content in plants must be compared to its content in the source from which the element has been supplied. Globally, the Earth's crust serves as a source of both titanium and molybdenum. One must therefore compare the abundances of these metals in the phytomass and the Earth's crust. Such an approach was used practically at the same time and independently by Polynov (1945), Thyssen (1942), and Hutchinson (1943). The two latter researchers made use of the data on elemental contents in dry organic matter. Such a procedure is not quite correct: the concentration of an element in the mineral mass of the Earth's crust is better compared to the element's concentration in the mineral part of plants, that is, in the ash. Following this line of reasoning, Polynov proposed to characterize the biological uptake of a chemical element as the ratio of its ash content to its crustal abundance. Perel'man (1975) has named this ratio the *Biological Absorption Coefficient* (K_b). As estimated in terms of K_b, molybdenum is accumulated by vegetation at a rate tens of times higher over that for titanium.

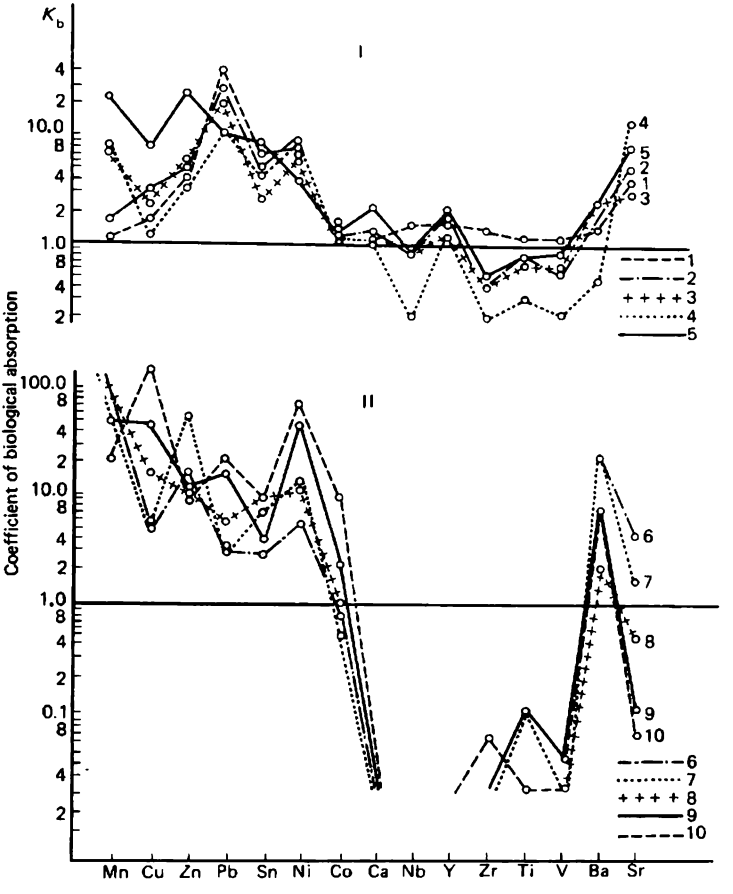


Fig. 1. Biological absorption coefficients (K_b) of trace elements plotted for different types of vegetation of the Kola Peninsula (Dobrovolsky 1983)

I, tundra vegetation: *1* — green mosses; *2* — lichens; *3* — rockfoil (of the family *Saxifraga*); *4* — low bush (*Vaccinium myrtillus*); *5* — grasses. *II*, northern taiga vegetation: *6* — spruce needles; *7* — birch leaves; *8* — low bush (*Vaccinium myrtillus*); *9* — grasses (aerial parts); *10* — grasses (underground parts)

Global K_b values for terrestrial vegetation are summarized in Table 1.6. They are illustrative of a strong differentiation of the involvement of elements in biological migration. The K_b values vary within a range of three orders of magnitude. In estimating the K_b values, the data in Table 1.5 and the average abundances of elements in the crustal granitic layer were used (see Table 2.2).

To a first approximation, all the elements may be divided on the K_b basis into two large groups. The first group is represented by elements whose ash concentration is greater than their crustal concentration. Of these, boron, bromine, iodine, zinc, and silver are taken up most actively. Their K_b values are greater than 10. Within this group, most elements have their K_b smaller than 10 but greater than 1: copper, molybdenum, manganese, strontium, lead, cobalt, nickel, and other metals. Their important physiological role is either unambiguously confirmed, or little doubted. To this group belong also mercury, selenium, and arsenic; despite their toxicity for animals even in very small doses, they are actively taken up by plants. This fact is at present poorly understood and requires further elucidation.

The second group comprises elements with low uptake exhibiting the K_b smaller than 1. Some of them occur in the Earth's crust in forms difficultly accessible to plants (gallium, zirconium, titanium, yttrium, lanthanum); others are toxic and for this reason their uptake is limited (fluorine, uranium).

It is noteworthy that the K_b for dispersed elements is independent of their crustal abundance. The abundance of zirconium in the "granitic" continental layer is several times higher over that of zinc, but the biological uptake of zirconium is smaller by about a factor of 13. This should be attributed to a poor involvement of zirconium in biological processes and to its occurrence in forms reluctant to the uptake by plants.

The outlined global geochemical trends in terrestrial vegetation appear to be supported by a solid physiological and evolutionary evidence. The results that have been obtained by the author in the course of his studies on dispersed elements in zonal vegetation types of the USSR show that the biological elemental uptake is maintained at a remarkably constant level despite variations in K_b for certain elements (Dobrovolsky 1969).

The specificity of zonal vegetation types is also discernible in the recorded general trends. For example, the taiga vegetation exhibits a sharp contrast between the trace element uptake ranging to 4-5 orders of magnitude, whereas in tundra vegetation, this contrast hardly exceeds 1-2 orders of magnitude (Fig. 1).

Unquestionably, the K_b value of a chemical element in different plant species may also exhibit a distinct behaviour. An element with K_b slightly larger or smaller than 1 may fall from the first into the second group, and vice versa. The K_b value for strontium is notably susceptible to variation. In some plants, the BAC for this element may drop down to 0.1 or even lower, whereas in others, it reaches as high as 20-30. The elemental biological uptake varies not only across the zonal vegetation types of the plains, but also in the altitudinal zonality of vegetation. A good example of this is the variation in the lead K_b of the deciduous parts of trees at different altitudinal zones of the Adzharo-Imeretinsky Mountain Ridge (Western Georgia, USSR). In subtropical piedmont

Table 1.6. Biological Absorption Coefficient and Annual Uptake of Trace Elements by Terrestrial Vegetation

Elements	Biological absorption coefficient	Annual phytomass growth uptake	
		per overall terrestrial area, thousand tons	per square kilometer, kg
Mn	6.86	41 400	345
Zn	11.76	5160	43.0
Sr	3.04	6020	50.1
Ti	0.20	5590	46.6
B	50.00	4300	35.8
Ba	0.66	3870	32.3
Cu	2.27	1376	11.5
Zr	0.88	1290	10.8
Rb	0.56	860	7.20
Br	36.36	688	5.70
F	0.10	602	5.00
Pb	1.50	215	1.79
Ni	1.54	344	2.87
Cr	1.03	309	2.58
V	0.39	258	2.15
Li	1.00	258	2.15
La	0.33	137.6	1.15
Y	0.42	137.6	1.15
Co	1.37	86	0.72
Mo	9.69	86.0	0.72
I	12.00	51.6	0.43
Sn	1.85	43.0	0.36
As	1.58	20.6	0.17
Cs	0.79	20.6	0.17
Be	0.80	17.25	0.14
Se	7.14	8.60	0.072
Ga	0.05	8.60	0.072
Cd	0.44	8.60	0.072
Ag	12.50	5.16	0.043
U	0.15	3.44	0.029
Hg	7.58	2.06	0.017
Sb	0.50	0.86	0.007

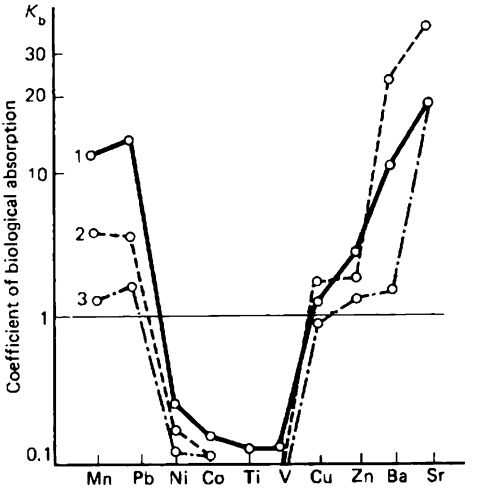


Fig. 2. Relative absorption of trace metals by the leaves of beech sampled in different vertical zones of the Adzharo-Imeretinsky Mountain-Ridge (Dobrovolsky, Kozarenko 1980)
1— zone of subtropical rain-fall piedmont forest; *2*—zone of beech-chestnut forests; *3*—zone of beech-spruce mountain forests

forests, the lead K_b value reaches 5-12; in beech-chestnut forest zone, it is 1.8-3.5, and in subalpine elfin woodland, about 0.5 (Dobrovolsky and Kozarenko 1980). In a notably spectacular manner this trend manifests itself in trees of the same species and genus growing in several altitudinal belts (Fig. 2).

1.5. Natural Biogeochemical Anomalies

The geochemical inhomogeneity of the continental Earth's crust exerts an appreciable effect on the vegetable composition. The elevated content of an element is accompanied by its increased concentration primarily in the photosynthetic organisms as the initial link of a food chain. Here, one can again see a qualitative distinction between the major and minor elements. Taken in quantitative terms, the former are the main building materials for plants, and their merely several-fold increase will result in a far-reaching rearrangement of the organism or, eventually, its complete dysfunction. The concentration of

minor elements is so insignificant that its increase even by a factor of several tens may leave no detrimental effects, although a definite response of the organism is to be expected.

The purely theoretical inference about a close relationship between the compositions of plants and rocks has found an important practical application. In plants that grow on the soils overlying ore deposits, the metal concentrations are noticeably higher than in plants growing on common soils. The effect of accumulation of dispersed metals in plants has constituted the basis of a biogeochemical method of prospecting for ore deposits. The method obtained an official recognition in May 1939, when a Swedish geologist N. Brundin took out a US patent No. 2158980 for prospecting of non-exposed ores through analyzing plants for metal content. Later on, the method has been updated owing to the efforts of many researchers, to name but few: A.P. Vinogradov, L.I. Grabovskaya, A.L. Kovalevsky, D.P. Malyuga, S.M. Tkalich (USSR), H. Cannon, H. Shacklette (USA), H. Warren, R. Delavault (Canada), J. Webb (Great Britain), K. Rankama, V. Marmo (Finland), R. Brooks (New Zealand), O. Nicolls (Australia), and others.

A number of ore deposits have been discovered applying the biogeochemical method. By way of example, the Endaco molybdenum deposit and the Bethlehem copper-molybdenum deposit in the British Columbia (Canada) were discovered through analyzing the needles and twigs of trees (Warren et al. 1971). In the South-East of the USA, a number of small-sized uranium deposits were discovered owing to the results of ash analysis of the genus *Astragalus*, twigs of trees and shrubs. Similar discoveries were made also in other countries, the USSR included.

The results of all those works have allowed us to arrive at a conclusion that the areas overlaying ore deposits are characterized by vegetation with abnormally high metal content, the so-called biogeochemical anomalies. These, although not outlining exactly the contours of ore bodies, give nonetheless indications of the ore occurrence.

The initial notion of metal uptake by plants was that the plants absorb water-soluble metal compounds to deposit them in the parts exposed to intense evaporation, mainly, in the leaves (Goldschmidt 1938). However, the currently available evidence has necessitated a substantial revision of the original concept.

It has been established that plants of different genera take up trace elements in a different manner; besides, the absorbed elements are deposited in the organs and tissues of plants nonuniformly. The content of trace elements in plants is very dynamic. First, the elemental concentration in the annually regenerating and dying-off organs increases in the course of vegetation period. Under common conditions, the concentration may change several-fold, and under the conditions of biogeochemical anomaly, much higher. Second, rains represent an essential factor since they wash off and leach trace elements from the leaves,

needles and young shoots. A heavy rain can reduce several-fold the concentration of trace elements in the leaves.

Along with its practical utility in prospecting for non-exposed ore bodies, each biogeochemical anomaly serves for a perfect testing ground enabling one to study the concentrational elemental effect on the state of plants. The biogeochemical anomaly makes it possible to follow the variation in concentration of an element from its background level common to the given locality to higher values and to compare the morphology and anatomy of the same species.

The involvement of minor elements in vital biological processes does by no means imply that the total of them as supplied to the organism will be assimilated to the best advantage. A certain amount of elements turns out to be in excess of the norm. Experimental studies by physiologists have shown that very high concentrations of trace elements in the nutrient solution cause damage to the plants, most commonly manifest in chlorosis of leaves. A small excess affects the metabolism in plants and induces adaptative alterations which can perpetuate through natural selection of many generations. These adaptations can either inhibit the involvement of trace elements in physiological processes, or, on the contrary, promote their participation in these processes. The excess trace elements for the most part form no tight bonds, are easily transported by cell sap and discharged into dying cells. Now, let us take a closer look at the dynamics of elemental distribution under the conditions of biogeochemical anomalies.

The transport of soil solutions in the tree starts at the root system and is effected through the conducting vessels of the sapwood. The rate of this transport is inhibited in the sapwood fibers with higher lignification. The transport of the sap carrying the photosynthetic products from the leaves is effected through the conducting bundles of the phloem whose died-off cells become incorporated into the bark. The excess trace elements are delivered not only to the deciduous organs (leaves, needles), but also to the dead tissues retained in the tree (xylem, corky bark).

Lagerverff and coworkers (Lagerverff et al. 1973) have studied experimentally the accumulation of lead in different parts of maize as a function of varied concentration of soluble lead salts in the soil. They have found that lead was increasingly accumulating in the stem nodes whereas its concentration in the inflorescences maintained at a constant level independent of the concentrational growth of lead in the soil.

The above examples provide evidence for an uneven distribution of excess minor elements in plants. Kovalevsky (1975, 1979) has proposed, on the basis of a large amount of experimental material, that in some plants (more exactly, in their definite organs and tissues) a hyperaccumulation of minor elements can take place without reaching seemingly any predictable limit. At the initial stage of this process, the accumulation of an element may prove to be a

stimulating factor for the biological activity and productivity of a plant; subsequently, the accumulation becomes inhibitory and may finally lead the plant to its death. In contrast, other plants are capable, after the concentration of an element has reached a definite level, of developing mechanisms counteracting further uptake of the element. Koval'sky has named these limiting levels the physiological absorption barriers and classified them into the barrier and the barrier-free types of absorption.

The limited uptake appears to be typical mostly of the green deciduous parts and reproductive organs of plants, whereas the hyperaccumulation is found in the roots, vegetable stem nodes, bark and, occasionally, the trunk wood of trees. Shown in Fig. 3 is the concentrational variation of lead in different parts of the plant as a function of lead concentration in the soil. One will observe that in the roots, the lead concentration rises from 0.001 to 0.1 % (on an ash-weight basis) with the increasing soil concentration of this element. Simultaneously, the lead concentration in the twigs of trees and the aerial parts of vegetable plants increases insignificantly to reach ultimately a constant level despite the ever-increasing lead concentration in the soil.

The elemental distribution in various plants exhibits specificity. In timber species native to Southern Armenia and confined to a molybdenum anomaly, the molybdenum distribution has been shown to be different. In hornbeam and maple, the molybdenum concentration in the bark is higher that in the leaves

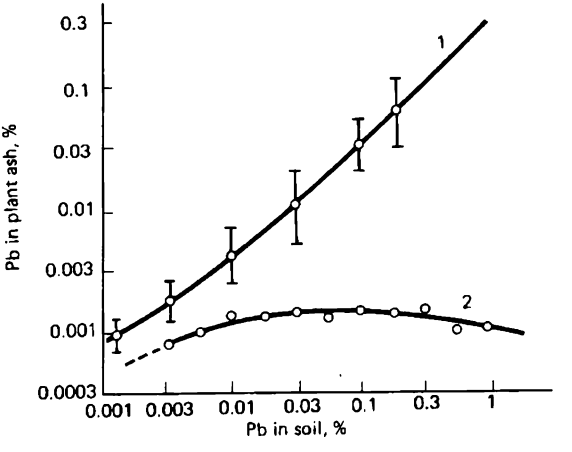


Fig. 3. Concentration relationships for lead contained in the soil and plant ash (Koval'sky 1979) *1*— average for the roots of 16 plant species; *2*— average for the tree twigs and the aerial parts of grasses

whereas in oak and snowball, the exact opposite is observed. In certain cases, the contrast of elemental distribution over vegetable organs and tissues goes in parallel to the growing environmental abundance of the element. The difference in background elemental concentration for various parts of a plant rarely exceeds a 10-fold level, whereas under the conditions of biogeochemical anomaly it can reach a 100-fold or even a higher level (Koval'sky 1979).

It follows from the foregoing that the concentration of minor elements in plants depends on a large number of diverse factors such as the abundance of elements in soil-forming rocks, mineralogic composition of bedrock, soil type, relief and ground water level, morphology and vegetation of plants, and others. For this reason, the concentrational distribution in sampled plants obeys the laws of statistics. The biochemists (Bowen 1966) and geologists (Koval'sky 1979) agree that most commonly the experimental distribution approximates a lognormal distribution. In geochemical anomalies, the contrast between elemental contents in various plants and in their parts becomes more sharp, which is reflected in an increased variability of concentrations. This effect has been suggested for use in biogeochemical prospecting for ores (Dobrovolsky and Rzhaksinskaya 1975).

In his studies of biogeochemical anomalies, Vinogradov focused attention on two points. First, within the confines of an anomaly all the plants exhibit, to a varied extent, the increased level of trace elements. Second, there are species distinguished by very high accumulated concentrations. The occurrence of such hyperaccumulator plants implies that the adaptation to abnormal conditions can develop not only through limiting the excess trace elements, but also through their increased uptake.

In various species, the adaptation proceeds differently. An interesting case was reported by Koval'sky (1974). In the arid landscapes of Armenia under molybdenum anomaly conditions, the widespread plants exhibited different concentrations of this metal. *Pyrethrum parthenifolium and Hypericum perforatum* (common St. John's wort) are poor accumulators of molybdenum. Besides, there is an uneven uptake from plant to plant. Over 60% of the sampled *P. parthenifolium* had molybdenum in the ash less than in the soil, and merely 29%, slightly greater. Simultaneously, in *H. perforatum* merely 12% of the samples exhibited a low concentration of molybdenum whereas its higher concentrations were found in over 70%. It is clear therefore that the adaptation of the said species quantitatively was not identical though following the same pattern, via limited uptake of excess trace metal. Along with those species, the locality had leguminous plants which accumulated molybdenum to high concentration.

Typical accumulators can develop endemic varieties that require definite trace elements in large amount and are therefore confined to localities rich in these elements. The products of weathering of ultrabasic rocks are heavily enriched

Fig. 4. Stunted form of two-leaved cinquefoil from the piedmont of Tannu-Ola Mountain-Ridge (Petrunina 1974)
1 — normal plant; *2* — modified plant; *3* — undeveloped leaf; *4* — short

with cobalt, nickel, copper, and chromium. On such bedrocks, a specific serpentine flora develops represented by *Pinus* species, rhododendron, and herbaceous plants. All of them are distinguished by a high concentration of the above elements. Along with the metallophilic flora concentrating simultaneously more than one element, there are known plants with a narrow geochemical specialization.

There is historical evidence that as early as the 17-18th centuries, the miners of Saxony employed in the mining industry of ore mountains were passing from generation to generation as a professional secret that certain plants indicated the occurrence of ores. There are known plants with a reputation of indicating zinc deposits, the so-called Galmei floras. One may refer to the most widespread of them as violet species (*Viola lutea*, var. *calaminaria*) and pennycress species (*Thlaspi calaminare*). Their ash contains 13-21% of zinc oxide, which is about 150 times the average ZnO level in the terrestrial vegetation. Endemic species that require a high concentration of tin form the tin flora (*Trientalis europaea, Gnaphalium suaveolens*, and others). The former of these species grows on the spoil heaps of old tin mines. In Catanga (the Republic of Zaire), endemic cobaltophils were found to grow on copper-cobalt ore outcrops. A representative of this cobalt flora, alyssum (*Alyssum bertolini*), also encountered in the USSR, was found to contain 7.86% of nickel. This is 1000 times higher than the average nickel content in plants. Known also are plants with a very high copper concentration, for example, those growing on the spoil heaps of copper mines, *Cyanotis cupricola*, and *Sopubia metallorum*

in Africa, copper mosses *Dryoptodon atratus*, and *Mielichhoferia* in Sweden, and gypsophila (Gypsophila patrinii) in Rudny Altai, USSR.

Plants that fail to adapt to high concentrations of soil metals develop teratological (monstrous) and stunted forms (Fig. 4). Commonly, developmental malformations are recorded in 10-20% of a given community; occasionally, 50% or even higher incidence was reported. Stunted and malformed specimens are either sterile, or the seeds produced from them are infertile. To a certain extent, morphological alterations are also observed in adapted plants; however, their generative organs develop normally, and the succeeding generations can retain the newly-acquired characters.

Also, the excessive trace element content does not leave the plant anatomy unaffected. Most commonly, the conducting system becomes affected. The strongest disturbances are observed in plants that failed to develop mechanisms enabling them to offset the elevated elemental concentration. Petrunina (1974) reported that excess chromium caused the contraction of cell size and the overall subdevelopment of conducting system. The high nickel content in stunted forms of *Linosyris tatarica* is reflected in the morphology of the leaf in whose cells chloroplasts undergo degradation. Under the action of high concentrations of lead and zinc, the conducting vessels and milk ducts in the poppy stem (*Papaver L.*) become squeezed and distorted.

The mechanism of morphological and anatomical alterations arising from high concentrations of trace elements is yet poorly understood.

It may be hypothesized that localities in the Earth's crust with high concentration of trace elements played a role in the speciation. In mountain regions, such localities are more common than in plains. Presumably, this has to a certain extent produced effects on the extensive floristic speciation in mountain regions, the fact first established by the famous Soviet genetist N.I. Vavilov (1887-1943).

2 Earth's Crust as a Factor in the Chemical Composition of Living Matter

The outer Earth's shells are related not only spatially, but also genetically. The origin of the shells, their compositional buildup and evolution are irrevocably intertwined. This relationship is to a significant extent due to the fact that the exterior part of our planet is subject to the geochemical activities of living matter. Many essential features of the World's land biogeochemistry have been shaped under the influence of the Earth's crust composition.

2.1. Earth's Crust Composition: Conceptual Survey

Chemists and petrographers, starting from the latter part of the 19th century, were busily engaged in the study of mineral composition of crustal rocks using gravimetric and volumetric methods of chemical analysis. Based on the results of numerous analyses of rocks, F. Clarke was the first to indicate the predominance of eight chemical elements in the Earth's crust: oxygen, silicon, aluminium, iron, magnesium, calcium, potassium, and sodium. This main conclusion has been borne out by the results of further studies. To gain a deeper insight into the biogeochemical processes occurring within the confines of the World's land, it is necessary to know not only the crustal composition *in toto*, but also the composition of the continental crust which is appreciably distinct from the oceanic crust forming the bed of oceans. The data summarized in Table 2.1 give an idea of the evolution of our knowledge about the average composition of the Earth's crust.

Given in column 2 are the data according to F. Clarke. These were estimated on the basis of an arbitrary crustal depth of 10 miles (16 kilometers); the analytical data used were those sampled mainly on land rocks, that is, characteristic of the continental Earth's crust. Given in columns 3 and 4 are data that have been estimated taking into account the volume and density of the major types of rocks constitutive of the Earth's crust and not extending beyond the Mohorovicic boundary (M-boundary). Estimates have been made separately for the continental crust constituting the World's land foundation and for the Earth's crust as a whole.

A comparison of the data listed in Table 2.1 shows that the variations in estimates from different sources do not alter significantly the overall picture. As is seen, oxygen and silicon accounting for about 2/3 of the total of the Earth's crustal mass are the predominant elements.

Along with the above major elements, other elements revealed their occasional presence in rocks. Besides, it was an evident fact that present in the Earth's crust were metals which could accumulate in separate localities to form ore deposits. However, the chemical analytical methods of current use in the 19th century could not afford the determination of low elemental concentrations. Basically different analytical methods were needed.

A powerful stimulus to the study of chemical elements contained at small concentrations in the crustal matter came from the development of a much more sensitive technique, the spectral analysis. The new findings have allowed V.I. Vernadsky to formulate, with good reason, the principle of "ubiquity" of all chemical elements. In his report to the XII Congress of Russian naturalists and physicians in December 1909 he declared: "In each droplet and in each solid particle from the Earth's surface, we discover ever so more new elements as our studies become increasingly more refined... In a solid or a liquid particle is reflected, like in a microcosm, the overall composition of cosmos."*

The idea of the "ubiquity" of chemical elements has for a long time been viewed with a thinly disguised scepticism even by the well-reputed authorities in geochemistry. The main reason for this distrust resided in the fact that the elements contained in a sample in amounts below the level of sensitivity of a given method could not possibly be detected in analysis, which created an illusion of their complete absence. This circumstance has found its reflection in the current terminology. The terms "rare elements" (die seltene Elemente in German), "frequency" (die Häufigkeit in German) have gained acceptance in geochemistry. In fact, we have to deal not with a real rarity or a low frequency of occurrence of an element in samples, but rather with its extremely low concentrations that escape reliable determination by not adequately sensitive analytical techniques.

The low sensitivity of a method was a common impediment to the quantitation of an element and merely allowed to confirm its occurrence in "trace" amounts. Traditionally, in the geochemical literature of wide use have been the terms introduced by V.M. Goldschmidt and his colleagues in the 1930s: trace elements (die Spurelemente in German, and des éléments trace in French). Owing to the assidious efforts of the scientific geochemical community, in the 1920s, the general picture of the composition of the Earth's crust has acquired more definite outlines.

* V.I. Vernadsky. Zametki o rasprostranenii khimicheskikh elementov v zemnoi kore (Notes on Distribution of Chemical Elements in Earth's Crust). Selected Works, Vol. 1, AN SSSR, Moscow, 1954, p. 401.

Table 2.1. Average Composition of Earth's Crust

Components	Content, %			
	after Clarke, 1924	after Vinogradov, 1962	after Ronov and Yaroshevsky, 1976	
			in continental crust	in Earth's crust *in toto*
SiO_2	60.3	63.4	59.3	55.2
TiO_2	1.0	0.7	0.7	0.9
Al_2O_3	15.6	15.3	15.0	14.6
Fe_2O_3	3.2	2.5	2.4	2.4
FeO	3.8	3.7	5.5	5.9
MnO	0.1	0.1	0.1	0.2
MgO	3.5	3.1	4.9	5.4
CaO	5.2	4.6	7.2	8.1
Na_2O	3.8	3.4	2.5	2.4
K_2O	3.2	3.0	2.1	1.6
P_2O_5	0.3	0.2	0.2	0.2
Total	100.0	100.0	100.0	100.0

The famous Soviet geochemist A.E. Fersman (1883-1945) proposed the term "clarke"* meant to signify a unit of the average abundance of a chemical element in the Earth's crust or in other global and cosmic systems, expressed as a percentage; the term was coined in the honour of the American geochemist F.W. Clarke as a tribute to his pioneering works aimed at the quantitative estimation of the distribution of chemical elements.

The clarke is an important magnitude in geochemistry. An analysis in terms of clarkes allows one to gain a better understanding of the distribution of chemical elements in the Earth, in the Solar System and in the part of the Universe accessible to our observations.

2.2. Relative Abundance of Chemical Elements in the Earth's Crust

The first attempts to analyze the overall chemical composition of the Earth's crust have shown that the elemental proportions could not be

* The clarke is a term deeply rooted in the Russian-language geochemical literature. In the English-language literature, of common use is its equivalent, the average abundance, or simply abundance. In what follows, the latter is preferred throughout the book.

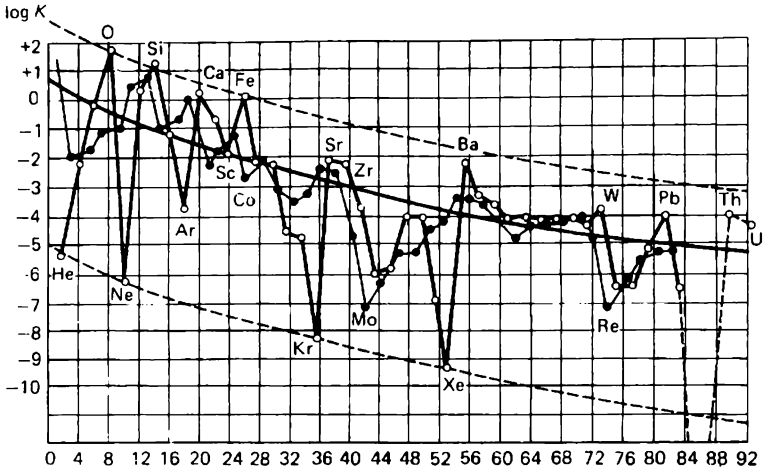


Fig. 5. Crustal abundances (clarkes) of chemical elements plotted on a logarithmic scale (Fersman 1932)

accidental. For one thing, there is a clearly observed tendency for the abundance of an element to decrease with the increase of the element's ordinal number, that is, its atomic mass. The trends in variation of the crustal abundances were clearly demonstrated by A.E. Fersman who plotted the logarithm of the elemental abundances as a function of the ordinal number of the elements (Fig. 5). One may see in this picture that the abundance of a chemical element decreases with its nuclear mass increasing, that is, as the atomic structure of the element becomes more complex.

The formation of the Solar System, Earth, and, finally, lithosphere was accompanied by variations in the ratios of their constitutive chemical elements. A major geochemical feature of the Earth's crust is uncommonly high oxygen abundance, which makes no analogy neither to the Sun, nor other stars. An explanation to this remarkable phenomenon must be sought not in the structure of oxygen nucleus, but in the ability of oxygen to form very tight chemical bonds with silicon, aluminium, and some other elements. In turn, silicon and aluminium form fusible compounds with alkalis. In the course of its geochemical evolution, the Earth's surface has shaped into a solidified alumosilicooxygen shell.

As is seen in Fig. 5, the crustal element abundances differ among themselves by greater than 10^9. These very large quantitative difference must reflect the qualitatively dissimilar roles the two groups of elements have played in the buildup of the Earth's crust. The most notable feature is that the first group

of elements occurring in relatively large amounts are capable of forming individual chemical compounds, whereas the second group elements with low abundances are dispersed, scattered about the chemical compounds of other elements. The elements of the first group are called the major elements, and those of the second group, the minor elements. Synonyms of the latter are also dispersed elements, rare elements, and trace elements — these, perhaps, being of more frequent use. An arbitrary bordering line between the two groups has been drawn at 0.1%, although the abundance of most trace elements is much smaller and goes down to thousandth or even lesser fractions of a percent.

The concept of the disperse state of chemical elements and their "ubiquity" was introduced into geochemistry by V.I. Vernadsky.

The overall chemical composition of the upper, also referred to as granitic, layer of the continental crustal block is listed in Table 2.2.

Any chemical compound to be formed requires the concentration of initial components to be in excess of a certain minimum below which the reaction becomes impossible. For this reason, predominant in the Earth's crust are chemical compounds made up of high-abundance major elements. Although the total number of natural chemical compounds (minerals) approximates some three thousand species, the number of minerals that constitute rocks as major constituents of the lithosphere is comparatively small. Over 80% of crustal mass is represented by silicates of aluminium, iron, calcium, magnesium, potassium, and sodium; about 12% is accounted for by silicon oxide. All these minerals are crystals, which determines the general features of crystal chemistry of the Earth's crust.

As shown by V.M. Goldschmidt, the silicate composition and crystalline structure of the Earth's crust are quite important factors in the distribution of trace elements.

The fact that the rock-forming minerals are made up of a limited number of chemical elements does not by any means imply that their crystal chemical structure is simple. Structurally, the silicates are very diversified. Their basic structural element is a group of four oxygen anions surrounding the central silicon cation. Four negative valencies of this silicon-oxygen tetrahedron are either compensated for by additional cations, or are involved in the buildup of rings, chains, bands, sheets, and three-dimensional frameworks. The cations that counterbalance the negative charge of Si-O tetrahedrons have a definite radius. Therefore, given a real crystal chemical structure, its constitutive elements can be only those whose ionic radii have an appropriate value.

The formation of widespread minerals is accompanied by a kind of sorting of trace elements. To illustrate this process, let us turn to a mineral of wide occurrence, feldspar. Its crystal chemical structure is made up of groups composed of three silicon cations and one aluminium cation, each being linked to four oxygen anions. The group as a whole represents a complex anion whose

Table 2.2. Chemical Element Abundances for the Granitic Layer of Continental Crust (in decreasing order of magnitude)

Element	Atomic number	Average abundance, $1 \cdot 10^{-4}$%	Element	Atomic number	Average abundance, $1 \cdot 10^{-4}$%
O	8	481000	B	5	10
Si	14	399000	Sm	62	9
Al	13	80000	Gd	64	9
Fe	26	36000	Pr	59	7.9
K	19	27000	Co	27	7.3
Ca	20	25000	Dy	66	6.5
Na	11	22000	Cs	55	3.8
Mg	12	12000	Er	68	3.6
Ti	22	3300	Yb	70	3.6
H	1	1000	Hf	72	3.5
P	15	800	Sn	50	2.7
F	9	700	U	92	2.6
Mn	25	700	Be	4	2.5
Ba	56	680	Br	35	2.2
S	16	400	Ta	73	2.1
C	6	300	As	33	1.9
Sr	38	230	W	74	1.9
Rb	37	180	Ho	67	1.8
Cl	17	170	Tl	81	1.8
Zr	40	170	Eu	63	1.4
Ce	58	83	Tb	65	1.4
V	23	76	Ge	32	1.3
Zn	30	51	Mo	42	1.3
La	57	46	Lu	71	1.1
Y	39	38	I	53	0.5
Cr	24	34	Tu	69	0.3
Nd	60	33	In	49	0.25
Li	3	30	Sb	51	0.20
N	7	26	Cd	48	0.16
Ni	28	26	Se	34	0.14
Cu	29	22	Ag	47	0.048
Nb	41	20	Hg	80	0.033
Ga	31	18	Bi	83	0.010
Pb	82	16	Au	79	0.0012
Th	90	16	Te	52	0.0010
Sc	21	11	Re	75	0.0007

constituents are eight oxygen ions, three silicon ions, and one aluminium ion. The group bears a net negative charge −1 which is counterbalanced by a monovalent potassium cation. This results in the buildup of a three-dimensional structure whose composition corresponds to a formula of $K[AlSi_3O_8]$.

The potassium ion radius is 0.133 nm. The site of a potassium ion in a crystal structure can accommodate a cation of commensurate size only. A good candidate is the divalent barium cation with its radius of 0.134 nm. Barium is much less abundant than potassium. Commonly, it occurs as an admixture to feldspar. On rare occasions, it can accumulate in large concentrations to form a rare mineral celsian, $BaAl_2Si_2O_8$.

In a similar manner, the widespread minerals and rocks can selectively retain chemical elements which, being present in small concentrations, are incapable of forming individual minerals. The mutual replacement of different ions in a crystal structure owing to their closely sized radii is called the isomorphism. This phenomenon has been known as early as the beginning of the 19th century, but its importance for global differentiation of dispersed chemical elements has become recognized only in the current century. Owing to isomorphism, the trace elements concentrate in an orderly manner in definite minerals. Feldspars harbour barium, strontium, lead; while olivines host nickel and cobalt, zircons, hafnium, and so forth. Elements such as rubidium, rhenium, and hafnium are incapable of forming individual compounds in lithosphere and occur exclusively as dispersed species in the crystal structures of host minerals. V.I. Vernadsky noted to that effect that minerals conceal behind the formulas we write for them myriads of dispersed atoms. Diverse isomorphs constitute an important factor in the differentiation of chemical elements with low abundance in the formative process of crystal matter of the Earth's crust.

2.3. Forms for Occurrence of Chemical Elements in the Earth's Crust

As has been shown above, the bulk of major crustal elements occur as individual chemical species which are the rock-forming minerals. Elements of low abundance are mostly dispersed in these minerals. Isomorphs are not the only form for the occurrence of trace elements. The phenomenon of crustal dispersal of elements manifests itself in various forms at different dispersion levels.

The coarsely-dispersed form is typified by well-crystallized small (commonly not exceeding 0.01-0.02 mm in diameter) accessory minerals. They are present as mechanical inclusions in rock-forming minerals. Although the relative content of accessories is not significant, the concentration of elements dispersed therein

is high enough to provide for the formation of individual compounds. For example, occurring in crystalline rocks in the capacity of accessories are zircon $Zn[SiO_4]$, rutil, less frequently anatase and brookite (trimorphs of common formula TiO_2), apatite $Ca_5[PO_4]_3F$, magnetite $Fe^{2+}F_2^{3+}O_4$, ilmenite $FeTiO_3$, monazite $CePO_4$, xenotime YPO_4, cassiterite SnO_2, chromite $FeCr_2O_4$ and other minerals of the spinel group, minerals of the columbite group $(Fe, Mn)(Nb, Ta)_2O_6$, and some others. The content of accessories in certain rock-forming minerals, especially, micas, may be quite high.

In certain minerals, mostly among sulfides and their congeners, of wide occurrence are structures produced from degraded solid solutions, finely-dispersed precipitates of a guest mineral in the host mineral. These may be exemplified by "emulsified impregnations" of chalcopyrite $CuFeS_2$ and stannite Cu_2FeSnS_4 in sphalerite ZnS, thin lamellar precipitates of ilmenite $FeTiO_3$ in magnetite $Fe^{2+}F_2^{3+}O_4$, finely-grained precipitates of silver minerals in galena PbS. This results in the occurrence of appreciable admixtures of silver in lead sulfide, tin in copper sulfide, and titanium in magnetite.The application of the polarization microscope to the study of thin sections has enabled one to identify in minerals not only minute solid inclusions, but also microvoids filled with remnants of the solutions from which the minerals were crystallized. This phenomenon, first signalled over a century ago by the founder of optical petrography H.C. Sorby (1826-1908), is at present well studied. The microcavities in minerals commonly contain liquid and gaseous components, occasionally with finely-grained crystals added. The problem of liquid inclusions has in detail been analyzed by Newhouse (1932) who reported the occurrence of heavy metals in the liquid as much as several percent. Part of guest trace elements readily extractable from finely divided monomineral samples is associated with

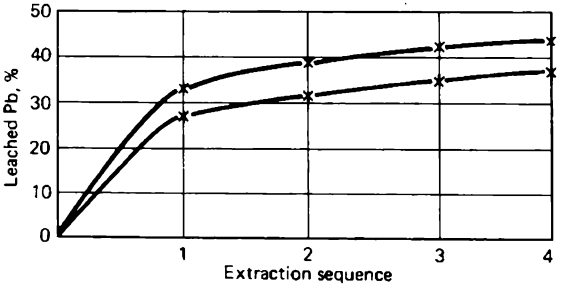


Fig. 6. Leaching of trace lead out of two garnet specimens by sequential extractions (Tauson 1964)

Table 2.3. Lead Concentration in Minerals Constituting Dzhumgol Ridge Granites (after Tauson 1961)

Mineral	Mineral fraction, %	Lead concentration in mineral, mg/kg	Total lead concentration in rock	
			mg/kg	%
Quartz	35.3	4	1.4	5.4
Feldspar	59.5	40	23.8	91.5
Biotite	3.7	20	0.7	2.7
Magnetite	0.7	17	0.1	0.4
Total	—	—	26.0	100.0

liquid inclusions. Ermakov (1972) studied microinclusions in fluorite and found $n \cdot 10^{-1}$% of zinc and manganese, $n \cdot 10^{-2}$% of barium, chromium, copper, nickel, and lead, and $n \cdot 10^{-3}$% of titanium. Further studies revealed the occurrence of lead, zinc, copper, silver, tin, lithium, and barium in liquid inclusions.

More sensitive analysis and the use of electron probing technique have shown that all rock-forming minerals contain trace elements in a highly-dispersed form which escapes detection not only by conventional optical microscopy, but also more sophisticated electron microscopy. In such systems, the dispersal of elements is effected at the ionic and molecular levels. The forms of such dispersal are not confined merely to the aforementioned isomorphism. There have been reported numerous minerals in which the occurrence of trace elements showed no relevance to isomorphism.

The wealth of analytical evidence obtained world-wide during the last three decades allows one to safely affirm that all of the rock-forming minerals proffer, figuratively speaking, harbourage to trace elements. Precisely these minerals contain most of trace elements present in the Earth's crust. If the proportion of host minerals and their concentration of trace elements are known, one can solve the problem of elemental balance for a given rock. For example, it has been found, in studying the Tien Shan granites that quartz, despite the seemingly negligible concentration of guest lead, accounts for over 5% of the total of this metal contained in the rock (Table 2.3).

It seems highly improbable that lead, zinc or any other metal can enter isomorphically into the structure of quartz composed of silicon and oxygen ions. Nonetheless, quartz serves as a host for many trace elements. A special method has been designed for estimating the potential utility of rocks and veins as ore deposits through analyzing quartz for lithium, rubidium, and boron content.

In experimental studies of adhesive strength of trace elements in rock-forming minerals, an unusual effect was discovered. It has been established, that when a finely divided mineral material is treated with sequential portions of weak acid-alkaline solvents, a significant part of the trace metals is easily extracted by the first portion of the solvent, without affecting the crystal structure of the mineral. In subsequent treatments, the amount of extracted metals decreases sharply, or the extraction becomes ineffective altogether (Fig. 6).

This finding has allowed one to make a proposal that part of the trace elements do not constitute the crystal structure proper and are rather associated with crystal defects. Such defects in real crystals are microcracks of various kind, unobservable in the optical microscope. The ease with which the trace metals are extracted is explained by the fact that these metals, localized at crystal defects, are held on the crystal by Van der Waals forces (Tauson 1961; De Vore 1955; Goni and Guillemin 1964). In rock-forming silicates, this method for the occurrence of trace metals accounts for 10-20% of the total of trace metals. In particular, the loosely-held form of lead in the Tien Shan granites makes up to 12-18% of the total of dispersed lead.

As a brief summary to the above overview, the following forms for the occurrence of trace elements in the crystalline crustal matter may be formulated:

A. Micromineralogic forms:

1. Elements constitutive of accessory minerals.
2. Elements contained in microscopic precipitates as produced by degradation of solid solutions.
3. Elements contained in residual solution inclusions.

B. Nonmineralogic forms:

1. Elements adsorbed at the defect surface of real crystals.
2. Elements isomorphically constitutive of the host mineral structure.
3. Elements disorderly incorporated in the host mineral structure.

The contributive role of the above forms for the occurrence of trace elements is markedly influenced by a variety of factors. Accordingly, the overall content of trace elements in different areas of the Earth's crust is liable to variation. Therefore, in order to obtain an objective estimation of elemental content, the methods of mathematical statistics are used.

2.4. Characterization of Chemical Element Distributions in the Earth's Crust

A vast variety of independent factors are responsible for the varied content of an element in different samples. If the distribution of a magnitude is determined by a sufficiently large number of roughly equipotent and mutually

independent factors, the distribution is said to obey the so-called normal, or Gaussian, law. Graphically, it is represented by a bell-shaped curve symmetric with respect to its maximum median ordinate. In normal distribution, the most probable value is the arithmetic mean ($\bar{x}$) which is coincident with the most frequently occurring values of the mode (in this particular case, the mode signifies the average mineral composition of a rock, usually expressed as percentage of total weight or volume). The symmetric spreading of a normal curve along the abscissa axis, that is, the scatter in values on both sides of the mode is characterized by the standard deviation denoted σ.

The normal distribution applies also to the logarithm of a magnitude and is termed then the logarithmic normal (lognormal) distribution law. In this case, the mode coincides with the geometric mean, and the spread in values is characterized by the logarithm of σ.

In 1940 N.K. Razumovsky found, in a purely empirical way, that the metal content in ores corresponded to a lognormal distribution. Ahrens (1954, 1964) has analyzed an ample experimental material and established, independent of Razumovsky, that the distribution of trace elements in magmatic minerals approximates the lognormal law. Numerous facts indicate that the distribution of high-abundance elements obeys the normal law, and that of trace elements, the lognormal law. This is another feature indicative of the basic distinction of major and minor elements.

The high variability of low-abundance elements is associated with their ability to reach very high relative concentrations. The maximum concentration for major elements may be greater by a factor of 10-20 relative to their average crustal abundance, whereas for trace elements, by a factor of 10^2-10^3, or even larger. For example, in minable ore depositions, the concentrations of lead, nickel, and chromium are as high as $100n$, and those of molybdenum and cobalt, $1000n$.

Speaking about the enormous mass of heavy metals confined to ore deposits, one should be aware that this mass is in fact a very small fraction of the total amount of metals dispersed in the Earth's crust. In particular, the commercial world reserves of zinc, copper, lead, and nickel ores accounts merely for thousandth fractions of a percent of the total mass of these metals dispersed within an upper layer 1 kilometer deep of the terrestrial continental crust.

The ore deposits communicate with the environmental rocks through compositionally variable zones. The ore body may be imagined as enclosed within an envelope of gradually diminishing metal concentration. Such formations have been named the halos of dispersion. The primary, syngenetic ore halos originate simultaneously with the ore bodies by the same formative processes. They exhibit a diversified configuration depending on the geological structure, composition of enclosing rocks, and the conditions for ore formation.

In ores, along with one or more major (essential) ore-forming elements, there are present associated elements in relatively elevated concentration, however, not in excess of the major element concentration. These companion elements are usually capable of replacing isomorphically the major ones. For example, cadmium is a permanent resident in zinc ores, as well as indium, gallium, and germanium present in smaller amounts. Copper-nickel ores contain cobalt as an appreciable admixture, also smaller amounts of selenium and tellurium. All these associated elements tend to diffuse around the ore body. Each exhibiting a different geochemical mobility, they form transitional zones of varied extension. The resultant effect is that the halos of dispersion are very complex, both compositionally and structurally.

The average abundance of a chemical element represents a norm, a geochemical background for a particular mineral type in a definite locality. Against the geochemical background, geochemical anomalies are distinguished, that is, areas of rock massifs with elevated concentration of trace elements. If these areas are associated with ore deposits, they may be regarded as halos of dispersion. If the metal concentration fails to reach a minimum required for ore formations, the respective anomalies are referred to as false. In treating statistically large-scale analytical data, one can follow the spatial alterations of geochemical background and reveal geochemical provinces. Within the confines of such a province, the rocks of one type exhibit consistent statistical parameters, primarily the average abundance of one or more trace elements. Rocks of the same types but originating from different geochemical provinces can differ severalfold among themselves in the average abundance of certain elements. Simultaneously, the major elemental composition of the rocks either remains the same, or varies very slightly. For example, in granites of different provinces with practically the same amounts of silicon, aluminum, iron, potassium, the levels of tin, lead, molybdenum, and uranium may differ by a factor of 2-3 (Tauson 1964).

It follows from the above that the nonuniformity of trace element distribution in the Earth's crust is a well-established fact. Therefore, in estimating the lithospheric abundance of elements *in toto*, one must take into account the ability of elements to concentrate or to disperse in different sample types — in rocks of different type, in rocks of the same type but originating from different geochemical provinces, in ores, and so forth. In order to quantitate the nonuniformity of elemental distribution in the Earth's crust, Vernadsky suggested a special index, the clarke of concentration, C_c. It characterizes the departure of the concentration of an element within a given volume from the crustal abundance of this element:

$$C_c = A/K,$$

where A is the concentration of a chemical element in rock, ore, mineral, or any other medium, and K is the crustal abundance of this element. If the clarke of concentration for an element is greater than 1, the medium is enriched in this element; if it is less than 1, the medium is depleted of the element in comparison with its crustal abundance.

Departures from the global or local geochemical norms and the concentrational alterations of chemical elements in space are not exceptions, but rather a specific feature of geochemical structure of the Earth's crust. This is of exceptional importance for the biogeochemistry of the World's land taking into account that rocks are the major source of chemical elements involved in the biogeochemical cycles.

3 Biogeochemistry of Atmosphere and Natural Waters of Land

The evolutionary buildup of the Earth as a planet proceeded through formation of structural zones. A major process at the initial developmental stages was the planetary differentiation of chemical elements. As is commonly believed, this process has resulted in the formation of a heavy core and a silicate mantle. The isotope analysis evidence has provided a good reason to presume that the outer phase shells — solid, liquid, and gaseous — also formed at the early stage of the planet's development.

The aggregative individualization of the outer shells does not necessarily mean that their stable chemical composition was the result of a single event. Starting from the earliest stage, their compositional evolution was an incessant process in which the living matter had played a pivotal role. Specifically, the compositions of the atmosphere and its inalienable counterpart hydrosphere have proved to be the most susceptible to biogeochemical processes.

3.1. Biogeochemical Evolution of Atmospheric Composition and the Gas Mass Exchange

The history of the atmosphere buildup provides a spectacular example of the impact by living matter on environment. The evidence of recent years indicate that the actual composition of the Earth's gas shell has been the ultimate stage of a long-lasting process in which a major role was assigned to the geochemical activity of living organisms.

The mass of the atmosphere is about $5.27 \cdot 10^{15}$ tons (Voitkevich 1986). The major fraction of gaseous matter (about 80%) is confined to the troposphere whose upper equatorial boundary reaches as high as about 17 km lowering down to 8-10 km at the poles.

The upper region of troposphere, the tropopause, is characterized by a sharp temperature drop and the absence of water vapours. The troposphere is the domain for active interaction of atmosphere with ocean and land, and it contains the bulk of water vapours and air-borne particulate matter. Photochemical reactions of exceptional importance for biosphere take place in the troposphere.

Beyond the tropopause, in the regions stretching across the stratosphere and mesosphere, the gas rarefication becomes increasingly more pronounced, and the thermal conditions become subject to complex variations. At a height of 25-30 km, the oxygen molecules suffer photodissociation by the action of solar radiation to form ozone. Ozone is very rarefied in the atmosphere. The atmospheric ozone, when exposed to the conditions common to the Earth's surface, at a pressure of 1 atm (101325 Pa), would have been confined to a layer of thickness less than 1 cm. Nevertheless, this very rarified atmospheric ozone absorbs 97% of ultraviolet solar radiation. Devoid of this shield, life on the terrestrial surface would have been doomed to extinction.

Distant to 80-100 km from the Earth's surface is the ionosphere, a region of highly rarefied and ionized gas. The outermost belt of the gas shell, the exosphere, extends as far as 1800 km. In the exosphere, the dissipation occurs, that is, the loss by the Earth of the lightest gases, hydrogen and helium, into space.

The Earth's gas shell composition as well as the ocean's composition are to a significant extent determined by the activity of living organisms and are maintained owing to a system of biogeochemical cycles. At present, 99.8% of the gaseous matter of atmosphere is nitrogen, oxygen, and argon (Table 3.1). Among the atmospheric components present in small amounts one may mention water vapour, inert gases and compounds produced by biological processes and photochemical reactions. The geochemistry of inert gases is of particular interest for the historical reconstruction of the atmosphere. The relatively high percentage of argon is associated with the fact that most of this gas is represented by the ^{40}Ar isotope derived from decay of the widespread ^{40}K. The amount of atmospheric helium is, by contrast, smaller by a factor of 1000 as might have been expected. This is due to the continuous extraatmospheric dissipation of this element. The rest of inert gases are present in the amounts in which they evolved during the entire period of Earth's existence. An analysis of the isotopic xenon proportion has brought the researchers to a conclusion that the gas shell emerged during a very short period of time which was roughly coincident with the period of Earth's accretion (Shukolyukov 1988). As is currently presumed, the short-term formation of the atmosphere was mainly due to a vigorous gas evolution as produced by intense meteorite bombardment of the Earth's surface.

Components of the primordial atmosphere were water vapours, CO_2, N_2, H_2, H_2S, CO, CH_4, HF, and HCl. The CO_2 content was not too high to enforce, via "greenhouse effect", the eventual evaporation of the World's ocean. Presumably, nitrogen was predominant. The gases as evolved from the Earth's interior (except inert gases) were represented, similar to the volcanic emanations of present days, by reduced or suboxidized species. One can conceive an idea on the primordial atmosphere composition by analyzing the eruptive volcanic gases (Table 3.2).

Table 3.1. Chemical Composition of Atmosphere (after Voitkevich 1986)

Components	Content (% by volume)	Mass, 10^9 tons
Dry air	100	5.12×10^6
N_2	78.08	3.87×10^6
O_2	20.95	1.18×10^6
Ar	0.93	6.59×10^4
CO_2	0.032	2.45×10^3
Ne	1.82×10^3	6.48×10
He	5.24×10^{-4}	3.71
Kr	1.14×10^{-4}	1.69×10
Xe	8.7×10^{-6}	2.02
CH_4	1.5×10^{-4}	≈4.3
H_2	$\approx 5.0 \times 10^{-5}$	≈0.18
N_2O	$\approx 3.0 \times 10^{-5}$	≈2.3
CO	$\approx 1.2 \times 10^{-5}$	≈0.59
NH_3	$\approx 1.0 \times 10^{-6}$	≈0.03
NO_2	$\approx 1.0 \times 10^{-7}$	≈0.0081
H_2S	$\approx 2.0 \times 10^{-8}$	≈0.0012

The solar radiation induces a dissociation of atmospheric water vapors. The continuous removal of the main reductant, hydrogen, by dissipation had resulted in the ever-increasing accumulation of oxidants. Two major consequences stemmed therefrom. First, a shield was gradually forming capable of protecting the Earth's surface from ultraviolet radiation. Second, this provided conditions for interaction between the reduced emanations continuously supplied from the mantle and the oxidants of photochemical origin which were replenished owing to hydrogen dissipation. This interaction, cyclic in nature, has predetermined the evolution of incoming biogeochemical cycles.

Signs of activity of the primitive forms of life have been recorded in the ancient geological formations. For example, one may refer to the Isua complex in Western Greenland found to contain organic compounds and iron oxides 3.8 billion years old; also, carbonaceous shale at Onvervacht, of Swaziland series in South Africa, aged 3.4 billion years. In siliceous formations of Warawoona (Western Australia) estimated as being 3.5 billion years old stromatolites (structures produced by communities of cyano bacteria) have been found.

The ancient biotic processes occurred in aqueous medium in the presence of a free oxygen, to which the laminated iron-oxide quartzites of Isua bear witness. Probably, the free oxygen was not initially omnipresent, and its occurrence was rather localized.

Table 3.2. Composition of Gases of the Great Tolbachinsky Fissure Eruption, Kamchatka (after Menyailova *et al.* 1980)

Components	Content (% by volume)	
	Water vapor included	Dehydrated
H_2O	78.56	—
N_2	11.87	55.36
O_2	0.01	0.05
Ar	0.06	0.30
CO_2	4.87	22.71
H_2	3.01	14.04
HCl	0.57	2.66
HF	0.056	0.26
CO	0.39	1.86
SO_2	0.03	0.14
H_2S	0.16	0.75
NH_3	0.11	0.51
CH_4	0.44	2.05
He	0.001	0.005

The most ancient biogeochemical processes appear to be connected to the biotic activity of chemolithotrophic bacteria. The microbiologists believe that thermophilic lithotrophic bacteria that thrive in hot springs at a temperature about 100°C (Brock 1978; Loginova 1982) may be regarded as analogues of a form of ancient life. Special microbiological studies of terrestrial and oceanic thermal springs have shown that currently there exist communities of thermochemolithotrophic bacteria which use the volcanic gases as a substrate. In the past, such microorganisms oxidized the reduced gaseous compounds and used the energy released by these reactions to synthesize organic matter. Certainly, this process did not lead to the production of oxygen. The chemolithotrophic communities that were assistant in the interaction of atmospheric oxidants with the reduced telluric gases signalled the first stage of geochemical activity of the living matter. The involvement of organisms in the global migration system — release of gases from the Earth's crust into atmosphere, their oxidation and subsequent uptake from the atmosphere — complicated the system and turn it from an abiogenic to a biogeno-abiogenic one.

The next stage was associated with the proliferation of cyano bacteria (blue-green algae) which made use of the solar energy, rather than the energy of oxidation-reductive chemical reaction, for the synthesis of organic matter. The

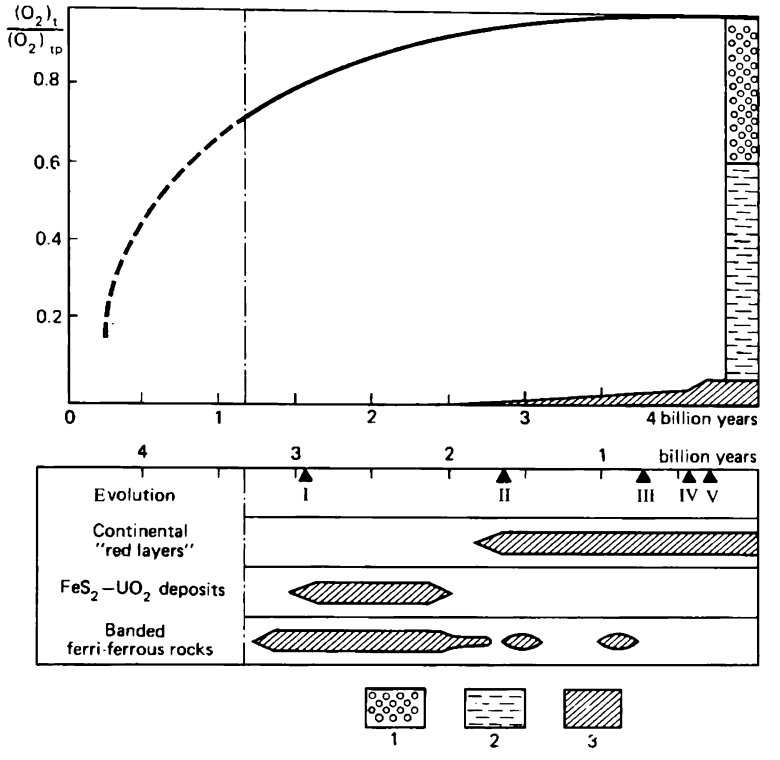


Fig. 7. Time-course of delivery and distribution of photosynthetic oxygen (after Schidlowski 1980). The ascending curve denotes biogenic production of oxygen; the vertical dashed-dotted line indicates the onset of rock deposition and formation of banded ferruginous limestone.
Life evolution periods: *I*—emergence of photoautotropic blue-green algae; *II*—emergence of eucaryotes; *III*—emergence of ancient marine multicellular fauna; *IV*—origination of terrestrial life; *V*—emergence of continental vegetation
Oxygen forms: *1*—oxygen bound in $[SO_4]^{2-}$; *2*—oxygen bound in Fe_2O_3; *3*—free molecular oxygen in the atmosphere-ocean system

photosynthetic reactions produced oxygen as a metabolite. Free oxygen is toxic to cyano bacteria, and they thrive only in its absence. The rapid spread of cyano bacteria in the ancient Ocean was favoured by the ability of oxygen to become easily bound into iron (III) oxides and sulfates. For this reason, despite the photosynthetic activity of cyano bacteria, the level of free oxygen in both ocean and atmosphere did not increase for a long period of time. Only after the total of divalent iron, dissolved in the ancient oceans, had become oxidized to form heavy layers of ferric quartzites (jaspilites), the accumulation

of atmospheric oxygen began. As estimated by Schidlowski (1980), of the total of photosynthetic oxygen, about 56% is bound as iron oxides, 39% as sulfates, and a mere 5% persists in a free state, distributed between atmosphere and ocean (Fig. 7).

The atmospheric oxygen started to increase 1.8-2.0 billion years ago. Following this was the formation of continental red rocks which bore witness to the fact that the oxidation of dissolved oceanic iron was in the main completed, and the oxidation of terrestrial iron began.

A biogeochemical specificity of the cyano bacterial system was the predominance of productive processes over destructive ones. The resultant effect was the burial of enormous amounts of organic carbon in the sedimentary deposits of ancient seas and the release of a 2.7-fold larger amount of oxygen into the atmosphere. The alterations in the geochemistry of ancient oceans and atmosphere laid grounds for a complicated evolution of biogeochemical cycles.

From a microbiological standpoint, the procaryota (as typified by bacteria and blue-green algae) are noted for high resistance and conservatism (Zavarzin 1984). The functional activity of the procaryotic system continued within a period of 1.5-2 billion years. About 1.4 billion years ago, the cyano bacterial communities started to be gradually replaced by algobacterial communities. Apparently, the accumulation of free oxygen in ocean and atmosphere played a decisive role in that process providing thereby for new conditions under which the competitiveness of cyano bacteria was not high. In the global process of organic matter buildup, the cyano bacteria became gradually replaced by algae. At the end of the Proterozoic (670-570 million years ago), a system of photosynthetic producers and animal consumers evolved, which set the stage for an oxygen-carbon biogeochemical cycle.

As follows from the above material, the formation of chemical composition of the atmosphere proceeded via regular differentiation of the chemical elements evolved from the Earth's interior in the form of reduced telluric gases. The system, abiogenic and cyclic in character, that had provided for the said differentiation, was a major and characteristic feature of the medium in which ancient organisms developed, each assigned a definite functional role in the system. Initially, the biogeochemical processes were involved as separate links in the system of global gas cycle in the atmosphere. In further course, with the emergence of new forms of life, the cyclic gas migration became increasingly dependent on the vital activity of organisms, which could not leave unaffected the composition of the atmosphere, ocean, and ancient terrestrial rocks. In turn, the changed ecologogeochemical conditions of the habitat influenced the development of organisms and made the biogeochemical cycles structurally more complicated. The emergence and subsequent widespread of the eucaryota has advanced the carbon-oxygen cycle to the foreground in the global system of biogeochemical cycles. Finally, the terrestrial higher plants

that evolved in the course of gradual expansion of living organisms on land became the major link of this cycle.

The biogeochemical processes that control the atmospheric levels of oxygen and carbon dioxide play a pivotal role in maintaining the normal environmental conditions. Free oxygen is a prerequisite for the existence of major forms of life, and carbon dioxide, while being the basic "building material" for photosynthesis, is also a factor which determines the thermal and climatic conditions on the Earth's surface (in reference to the "greenhouse effect").

According to the data by Bazilevich (1974) and Dobrodeyev (1976), the World's land vegetation, prior to active human intervention, had a mass of about $2.5 \cdot 10^{12}$ tons of dry organic matter. Carbon, given its content of 46% (Romankevich 1988), accounts for $1.15 \cdot 10^{12}$ tons of the total mass of terrestrial vegetation. To produce such an amount of vegetable carbon, $4.2 \cdot 10^{12}$ tons of CO_2 had been consumed, with the concomitant release of $3.1 \cdot 10^{12}$ tons of O_2 into the atmosphere. Deforestation and other effects of human productive activities have reduced the terrestrial vegetation by some 25%, with its mass at present being about $1.88.10^{12}$ tons of dry organic matter, of this, $0.865 \cdot 10^{12}$ tons of carbon. For the synthesis of organic matter of the extant vegetation, the required amount of CO_2 has been $3.172 \cdot 10^{12}$ tons, with the concomitant release of $2.307 \cdot 10^{12}$ tons of O_2 into the atmosphere.

The chemical elements that constitute the overall mass of terrestrial vegetation persist in a bound state for a more or less prolonged period of time. The dynamics of the mass exchange of gases within a period of one year may be characterized by the ratio of the mass of organic matter produced by photosynthesis to the mass of degraded organic matter.

The annual production of terrestrial vegetation prior to human activity was presumably about $170\text{-}180 \cdot 10^9$ tons. Carbon, given its content of 46%, accounts for 76 to $81 \cdot 10^9$ tons, or, on the average, for $80 \cdot 10^9$ tons. The annual requirement of CO_2 to produce such an amount of organic matter would have been $293 \cdot 10^9$ tons, with the concomitant release of $213 \cdot 10^9$ tons of O_2. If one takes into account that 15% of synthetic organic matter undergoes oxidation and degradation because of the respiratory activity of the plants, it becomes evident that additional $14 \cdot 10^9$ tons of carbon was involved in the annual production of vegetation. Since this amount of carbon is biochemically oxidized and converted to CO_2, it is of little importance for the ultimate balance of CO_2 and O_2 and is therefore ommitted from subsequent estimations.

With allowance of a 25% decrease made for human activity, it may be accepted, that the current atmospheric supply of CO_2 for the synthesis of the World·s land vegetation amounts to $220 \cdot 10^9$ tons per year; of this, the assimilated carbon is $60 \cdot 10^9$ ton/year and oxygen released into the atmosphere is $160 \cdot 10^9$ ton/year. These estimates are approximate and are liable to further refinement, but it is felt that the orders of magnitude, correspond to the actual state of things.

The gas metabolism in the system: living matter-atmosphere-living matter is cyclic in nature. The plants are incapable of synthesizing the organic matter in default of atmospheric carbon dioxide. By the photosynthetic reaction, the release of a certain volume of oxygen requires the absorption of the equal volume of CO_2. The bulk of terrestrial carbon dioxide is produced by microbiological degradation of organic matter. Most of carbon dioxide goes back to the atmosphere to be involved once again in the biological cycle. Therefore the ratio of the synthesized-to-degraded organic matter is a measure for the supply of oxygen to the atmosphere.

If the degradative processes consume the same amount of organic matter as produced by vegetation, the amount of oxygen supplied will never increase however great might be the rate of its production by vegetation: as much of oxygen as produced by photosynthesis will be consumed in degradation. An indispensable requirement for a higher level of oxygen in the atmosphere is the preponderance of the mass of synthetic production over the mass of degraded organic matter. Such a condition can be fulfilled only on land owing to the availability of mineral nutrition for plants. The situation in oceans is quite distinct where nutrients are scarse, and for this reason the degraded products from photosynthetic organisms are not eliminated from the biological cycle and are reutilized by different groups of consumers.

A comparison of the vegetable mass of the World's land ($2500 \cdot 10^9$ tons) with the annual production rate ($172 \cdot 10^9$ ton/year) reveals that the renewal of the terrestrial phytomass occurs on the average each 15 years. Certainly, for the tree vegetation this process is more lengthy than for the herbaceous. In ocean, the phytoplankton is renewed daily, and the total of living matter, within less than a month.

At the present time, there have been accumulated within the confines of the World's land about $0.7 \cdot 10^{12}$ tons of dry matter from nondegraded vegetable remnants (peat, forest litter) and also some $2.4 \cdot 10^{12}$ tons of humus. The distribution of living matter and nondegraded organic remnants on the land surface obeys the bioclimatic zonality. The largest phytomass is typical of rainfall forests, whereas the largest amount of dead organic matter is found in the belt of boreal coniferous forests.

The gases are not confined solely to the gas shell of the planet. The water bulk of seas and oceans contains $4.32 \cdot 10^{18}$ m^3 of dissolved gases. This volume is three times the total water volume of the World's ocean.

The troposphere and the surface layer of oceanic water coexist in a state of dynamic equilibrium. The amount of gases dissolved in water is dependent on temperature and water salinity. The solubility of gases in water increases with decreasing temperature. For this reason, the ocean in a cold season of the year absorbs gases from the atmosphere and releases them in a warmer season. Fresh water is a better solvent for gases than salt water. On the average,

1 liter of oceanic water contains the dissolved gases: nitrogen, 13 cm^3; oxygen, 2 to 8 cm^3; argon, 0.32 cm^3, and carbon dioxide, 50 cm^3. The much larger amount of dissolved carbon dioxide is explained by the ability of CO_2 to enter a chemical reaction with H_2O. The reaction yields carbonic acid and a readily soluble product of its dissociation, the anion $[HCO_3]^-$.

Thus, owing to the continuous absorption of gases by water and their subsequent release, the hydrosphere and atmosphere persist in a state of dynamic equilibrium. Water is also involved, through evaporation and condensation, in this cyclic global process.

The atmospheric water cycle involves over 520 thousand cubic kilometers of water per annum (L'vovich 1986). The importance of this global process can hardly be overestimated: this cycle is the major factor in the control of the thermal regime of the planet and in the providing of conditions for the existence of life. Simultaneously, the natural water, while being a chemical compound with definite physical properties, is also an active factor in the atmospheric migration of chemical elements. For this reason, the continuous displacement of enormous masses of water within the systems (i) land surface-atmosphere-land surface, (ii) ocean surface-atmosphere-ocean surface, and (iii) ocean-atmosphere-land-ocean is an important factor in understanding the geochemistry of the biosphere.

During the recent decades, the chemical composition of atmosphere has become an issue of special concern owing to its close relation to the so-called greenhouse effect which is in essence the shielding of the solar infrared radiation reflected from the Earth's surface. The trapping of the Earth's thermal radiation makes the air temperature rise, which may lead to global climatic changes potentially catastrophic for the terrestrial conditions.

A variety of gases and contaminants take part in the shielding of reflected thermal radiation (methane, nitrous oxide, ozone, freons, and others) but the major role is assigned to water vapors and carbon dioxide. Water vapors absorb most of reflected energy but leave unabsorbed the radiation at wavelength of 8 to 18 μm. This "transmission window" is in part blacked out by the atmospheric CO_2 molecules capable of absorbing the reflected radiation within a range of 12-18 μm. Methane and nitrous oxide absorb radiation in a shorter wavelength spectral region transparent to water vapors.

With a view to gain a better understanding of the dynamics of CO_2 and CH_4 supply to the troposphere, measurements have been taken at 17 meridionally located weather stations in coordination with the cosmic survey (Zavarzin *et al.* 1987). The data obtained have shown that the major sources of atmospheric supply of carbon dioxide and methane were the northern regions of Eurasia and North America. The maximum CO_2 concentration was recorded during the autumn-winter season, which should be attributed to the activity of fungal and bacterial microflora. The highest concentration of CH_4 was observed in the

midseasonal winter-spring period and was associated with the activity of anaerobic methane-producing bacteria.

Thus, the boreal belt on the World's land is the main supplier of major greenhouse gases, CO_2 and CH_4. Their production is closely related to microbiological processes occurring in the soil. The disturbance of natural equilibrium because of large-scale deforestation and the ensuing waterlogging leads to an increase of both the anaerobic microbiological activity and the emission of greenhouse gases into the atmosphere.

3.2. Geochemistry and Biogeochemistry of Aerosols

In much the same way as natural waters contain dissolved compounds and finely divided suspensions, the atmosphere contains free gas molecules and ions, and, in addition, atomized particles of solid and liquid substances.

Suspensions of solid and liquid particles in a gas medium are currently referred to as the aerosols. Solid aerosol particles play a very important role in meteorological phenomena acting as nuclei for the condensation of water vapors. The size of these particles ranges from several microns to hundredth and thousandth fractions of a micron. Particles of smaller size cannot exist separately and adhere to larger particles. Among the air-borne species, there are electroneutral and charged particles (ions). The latter are made up of neutral molecules clustered around an ion. Electroneutral particles measuring less than 0.1 μm (the so-called Aitken nuclei) are very large in number but, by virtue of their negligible size, they account for a mere 10-20% of the total aerosol mass.

Both the land and the ocean, persisting in a state of continuous cyclic exchange with the lower atmospheric layers, supply aerosol particles to the air and regain them as components of atmospheric precipitation, or as solid precipitation. The air-borne particles of continental origin are relatively large, their average size being 2-3 μm. Over the ocean, smaller particles are predominant sizing about 0.25 μm (Lisitsyn 1978).

On land, not only the evaporated surface waters, but also the disperse solid matter of lithosphere are involved in the atmospheric exchange processes. The aerosol particles of marine origin are mostly represented by water-soluble salts, whereas those carried away from the continental surface are small particles of soil, rock, and volcanic ash. According to the observations of Lisitsyn (1978), the fragments sizing 0.1-0.01 mm are commonly carried over in the lower layers of the troposphere to a distance of several hundred to a thousand kilometers. The particles sizing 1-10 μm migrate across the whole width of troposphere, the distance of their transport reaching 5-7 to 10 thousand kilometers.

The air-borne loess dust from the deserts of eastern Asia expands over wide areas of the continent reaching also quite distant regions of the Pacific. Its fall-out was recorded on the atolls of the Pacific Ocean and even on the Hawaiian Islands (Duce *et al.* 1980; Shaw 1980). The red dust, wind-blown off the surface of arid areas of Africa, is carried by the trade-winds to a distance of 2-3 thousand kilometers over the water area of the Atlantic Ocean. The sailors who took part in the first voyage of Columbus, were astonished to see the decks of their caravels covered with red African dust amid the boundless ocean. The estimates of the mass of soil dust blown off the continents into the World's ocean differ significantly. Garrels and MacKenzie (1974) cite a figure of 600 million tons; the estimate by Lisitsyn (1978) is much higher, 1.6 billion tons. To estimate quantitatively the total mass of solid particles torn away from the terrestrial surface into the atmosphere during a period of one year is at present an impracticable task. One may merely try to evaluate the amount of the most finely divided particles with a sufficiently long residence time in the atmosphere. Their mass has been estimated to reach billions of tons.

It has been found in the 1960s, that trace metals are present in large amounts in the troposphere. The concentration of air-borne trace metals is negligibly small: it is lower by a factor of 100 than that in natural waters, and by a factor of 10^6 than their crustal concentration. A convenient unit for expressing such small concentrations is nanogram per 1 m^3 of air. The highest trace metal concentration is confined to the lowermost layer of the troposphere, at a close proximity to the terrestrial or water surface. To better understand the distribution of air-borne chemical elements, profiling studies of the troposphere have been carried out in the USA and USSR. The analysis of air samples taken at different heights ranging from 15 to 50 km has shown that the bulk of trace elements is concentrated within a one-kilometer air layer above the Earth's surface. In the upward direction, the elemental concentration declines sharply by one or two orders of magnitude.

Both the content and the distribution of elements over continents and oceans are different. One may presume, at the level of our current knowledge, that in the lowermost air layer over the continental areas free of industrial contaminations, the elemental concentrations follow the order as shown below (in ng/m^3):

$n \cdot 10$: Zn > Cu > Mn > Cr > Pb > V > Ni > As;
n: Cd > Se > Co; Hg, 1-2; Sb, about 1; Sc, 0.1-1.0.

Therefore, an air column 1 km high over a land area of 1 km^2 contains any of the above metals in an amount of

$$1 \text{ to } n \cdot 10 \cdot 10^{-9} \text{ g/m}^3 \times 10^9 \cdot \text{m}^3 = 1 \text{ to } n \cdot 10 \text{ g}.$$

Thousand tons of metals and arsenic, and hundred tons of selenium, mercury, antimony are found within a one-kilometer air layer over the continents. Noteworthy, the above data refer to a pure natural phenomenon, independent of the productive activity of man.

Aerosol particles serve as carriers for trace elements. A close relationship between them is easily perceived in comparing the distribution of condensation nuclei (aerosol particles) and the aerial concentrations of heavy metals (Fig. 8). For this reason, the results as obtained through studying the dynamics and composition of aerosols provide valuable information about the atmospheric migration of chemical elements.

The supracontinental concentration of aerosol particles commonly measures tens of micrograms per 1 m^3 of air. An analysis of a large number of air samples taken over different regions of the World's ocean has shown the concentration of terrigenous mineral particles to vary from 0.4 to 14 $\mu g/m^3$, and that of salt particles, from 3.3 to 8.7 $\mu g/m^3$, the average total being about 10 $\mu g/m^3$

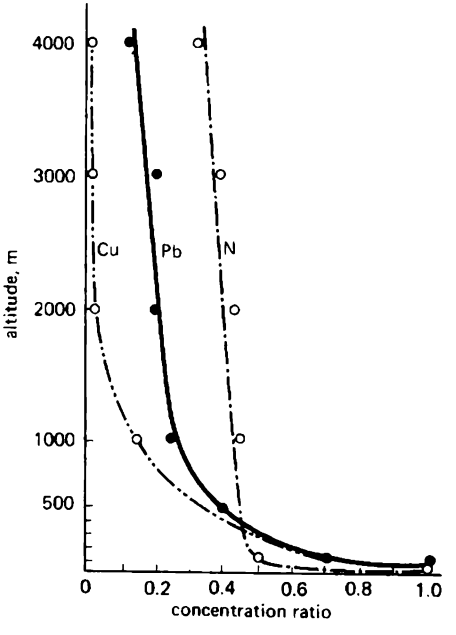


Fig. 8. Tropospheric distribution of heavy metals and condensation nucleai (Zhigalovskaya *et al.*). The x-axis scale is the ratio of the metal concentration at a given altitude to the metal concentration at a 50 m altitude from the surface; *N* is the condensation nuclear concentration

(Prospero 1979). The aerosol concentration in the littoral circumcontinental oceanic zone makes up an average of 50 μg/m^3 (Bezborodov and Eremeyev 1984). According to Junge (1956), the tropospheric concentration of condensation nuclei decreases rapidly to a height of 5 km, keeps roughly constant to 12 km, and above 12 to 16 km again tends to a rapid decline. Selezneva (1966) observed that the nuclei concentration at a height of 2 km decreased 10-fold as compared to that at a height of 250 m.

The air-borne particles can be removed from the troposphere either by gravitational sedimentation, or through atmospheric precipitation. American researchers have established, through making use of ^{210}Pb, ^{210}Bi, and ^{210}Po isotopes, that the average residence time for dust particles in the locality of Denver (State of Colorado, USA) is 4 days, whereas the smallest particles precipitable with the rain, persist in the atmosphere for 7 days. The available data allows one to infer that the residence time of air-borne particles ("aerosol life-time") over the continent varies within a period of 1 to 30-40 days, the average time being about 5 days.

Large aerosol particles never reside long in the air and soon fall back to the ground, in a close proximity of the site of their entrance into the troposphere. Particles sizing 3-5 μm or smaller become entrapped in the troposphere via ascensional circulation. In the tropical belt, their displacement is subject to the permanent trade-wind and seasonal monsoon circulations in the westward direction. In the northern and southern temperate belts, the atmospheric processes are prone to instability and are operative under cyclonic and anticyclonic conditions; still, the resultant direction of particle transport is essentially eastward. In the upper troposphere (above 7 km), jet streams are operative carrying the aerosols from west to east in the sublatitudinal direction. According to Lisitsyn, these jet streams in the arid zones are responsible for most of the aerosol transport. The extension of this transport is appreciably greater over that in the lower troposphere, the former reaching 5-7 thousand kilometers, or even more.

Although the bulk of aerosol migration is tropospheric, a very small part of air-borne particulate matter is entrapped in the stratosphere to persist there for 4 to 14 years. The stratospheric particles are 0.2-2 μm in size. Their transport is predominantly carried out westward by very rapid jet streams. No water vapors have been observed in the stratosphere. It is presumed that the removal of aerosols is effected through formation of sulfate flocculates which cluster around the particles ("sulfate wash-out"). The main dust fall takes place in arid and polar zones. As has been estimated (Lisitsyn 1978), the fall rate for stratospheric aerosols in the northern hemisphere is 2 to 32 mg/cm^2 per 10^3 years. Presumably, an equivalent amount of suspension enters the stratosphere.

Aerosols of continental and oceanic origin differ markedly in composition. The aerosols supplied to the atmosphere from the continental surface contain,

Table 3.3. Accumulation Factor for Trace Metals in Continental Aerosols (after Dobrovolsky 1980)

Trace metals	Accumulation factor K_a	Accumulation rate
Cadmium	> 100	Very high
Lead, copper	50-100	High
Zinc, copper, nickel, chromium	10-50	Medium
Vanadium	1-10	Moderate
Titanium	< 1	Negative

at a level of lithospheric abundance, typically terrigenous elements such as silicon, aluminum, iron, titanium, zirconium, yttrium, lanthanum, scandium. In the oceanic aerosols, dominant are the cationic elements of sea salts: sodium, magnesium, calcium, strontium. Simultaneously, typical of aerosols is the elevated concentration (relative to terrigenous chemical elements) of certain heavy metals and multivalent elements (arsenic, antimony, bismuth).

For a quantitative estimation of the selective accumulation of chemical elements in aerosols, the author has proposed to use the aerosol accumulation factor K_a (Dobrovolsky 1980):

$$K_a = A/K,$$

where A is the content of an element in the solid aerosol phase; K is the crustal abundance of this element in the granitic continental layer. The estimation is made on a solid aerosol basis. The pertinent data, summarized in Table 3.3, show that the concentration of some elements in solid aerosol particles increases by 1-2 orders of magnitude in comparison to their concentration in the granitic lithosphere layer (cadmium, lead, zinc), whereas the concentration of other elements varies less markedly (vanadium, titanium).

The elevated concentration of some elements in continental aerosols is due to a number of factors. One of these resides in the composition of the initial material for aerosol particles. If only minute fragments of rock material were blown away with wind, then the composition of aerosol particles would be identical to the lithospheric composition. However, susceptible to the carry-over by wind are not newly formed rocks, but loose products of soil and weathered rocks. In the upper horizon, the concentration of certain elements is rather high owing to their accumulation in plant remains, humus, or on the surface of argillaceous particles. The metal concentrations in continental dust and soil have been shown to be close. Thus, the disperse particles, carried over

from the land surface to the troposphere, can be initially enriched in a number of elements.

The mineral dust, contained in the lowermost near-ground tropospheric layer over ore outcrops contains elevated metal concentrations owing to the carry-over of loose weathered products enriched in ore elements. This phenomenon was made use of by Weiss (1967) in his aerogeochemical method of ore prospecting. The method consists in sampling the mineral dust by means of filters from the air at low height and in dispatching the collected samples for analysis. The tests that had been carried out in the northern regions of the Cape Province (South African Republic) showed that the air-borne dust over the ore deposits contained lead in concentration 5-10 times higher than that over sites outside the ore field.

As a rule, the loose products of weathering are enriched in metals appreciably less than the aerosols. As will be observed in Table 3.5, the concentration of certain heavy metals is hundreds of times higher over its respective lithospheric abundance. It may be presumed therefore that the enrichment of aerosols in such metals occurs in the troposphere.

Supportive evidence has been obtained from studies on the heavy-metal mass exchange in a system "land surface-troposphere-land surface". This will clearly be seen in analyzing the migration cycle for lead.

In loose products of weathering (soils) that constitute the surface layer of land and are exposed to winds, the lead concentration is about 20 μg/g. Given the average dust concentration in the troposphere 30 mg/m^3, 1 m^3 of air contains 0.6 ng of lead, whereas the entire terrestrial troposphere, except the glaciated areas, about 80-90 tons is expected. In reality, the lead concentration in continental aerosols is, as a rule, significantly higher, 30-50 to 100 μg/g, or even more. The aerosol accumulation factor for lead is commonly equal to 30-60. With reference to the above lead concentration in the solid aerosol phase, the lead level in nonpolluted air ranges from 0.9-1.5 to 3 ng/m^3 and, occasionally, higher. Given these concentrations, the lowermost tropospheric layer 1 km high above the ground level is expected to contain lead in amounts of 120-200 to 400 tons, or even more.

Thus, the difference between the mass of lead that may be estimated, on the one hand, starting from the metal concentration in loose products of weathering, and, on the other hand, from the lead concentration in solid aerosol phase, reaches several hundreds to 1-2 thousand tons. With allowance made for the cyclicity of dust migration in the troposphere, this difference will be still larger. Experimental studies using the ^{210}Pb isotope have shown that for the majority of dust particles as lead carriers, the period of complete renewal is commonly about 7 days (Francis *et al.* 1970). It is anticipated therefore that the cyclicity of dust migration in the system "land surface-troposphere-land surface" is about 50 cycles per year. As a result of continuous aerosol fall-out,

the annual "one-way" supply of lead to the World's land surface is $10 \cdot 10^3$ to $100 \cdot 10^3$ tons.

Within a world-wide research program of 1970-1980s, detailed studies of the fractional air composition of the lowermost troposphere have been carried out in many laboratories using micropore filters and post-filter vapor-gas trapping technique. The results of those studies were reviewed by Miklishansky *et al.* (1978). The chemical elements, dispersed in the troposphere were shown to occur in various forms, including a gaseous one. In the gaseous form not only easily sublimable elements (iodine, arsenic, mercury) were present, but also heavy metals such as zinc, copper, and lead are found. The above-mentioned elements make a part of the tightly bound composite aerosol particles smaller than 0.5 μm in size. Presumably, one may argue for the existence of a dynamic equilibrium for these elements involving their free state in the gas phase and their adsorption on the aerosol particles. At the same time, there are elements preferably concentrated in relatively large aerosol particles such as aluminum, iron, scandium, barium, lanthanum, yttrium, and a number of others.

The enrichment factors for aerosol elements as estimated with respect to the average crustal composition have shown that the relative concentration of elements occurring in a gaseous form increases drastically in ultrafine aerosol fractions. The relative concentration of elements, mainly confined to larger particles of 0.5-1.0 μm, varies insignificantly.

As an example, shown in Table 3.4 is the elemental distribution among variously-sized aerosol particles in the near-ground tropospheric layer over the

Table 3.4. Distribution of Chemical Elements Between Aerosol Particles and Vapor-Gas Phase in the Atmosphere of Sary-Chelek National Park, % of the Total Content of Each Element (according to Kulmatov (1988), supplemented data)

Element	Particle size, μm			
	> 1.0	1.0-0.4	Total > 0.4	< 0.4
Fe	37	55	92	8
Co	30	58	88	11
Sc	71	16	87	13
Cu	48	4	52	44
Zn	16	6	22	78
Hg	14	8	22	77
As	51	5	56	44
Br	22	16	38	62

mountain region of a Tien Shan ridge (Central Asia). The region is located in the southern slope of the Chatkal Ridge, at an altitude of 600 m above sea level and has the coordinates 41°06 N and 69°30 E. We wish to emphasize that the locality is situated within the confines of a nature reserve territory and is thus remote from potential sources of contamination. One will easily observe in Table 3.4 that most of the air-borne iron and scandium is present in aerosol particles larger than 0.4 μm, whereas most of the copper, zinc, and mercury is confined to smaller particles and in the vapor-gas phase.

Therefore, numerous chemical elements, heavy metals included, enter the troposphere in a gaseous form to be entrapped by small-sized aerosol particles and, as the latter precipitate, finally eliminated from the troposphere. Most clearly, the mechanism of this process is seen in the elements capable of easy evaporation. Mercury is a good example. This metal evaporates at any temperature recorded at the Earth's surface, down to the mercury freezing point –38°C. The mercury vapors easily diffuse through the soil and have no great difficulty in penetrating across a water layer.

As evidenced by aerial aircraft observations, the mercury vapor concentration at an altitude of 3 km is very low. At an altitude of 50 km above the ground level, the mercury concentration commonly ranges from 0.4 to $1.0 \cdot 10^{-9}$ g/m^3 (Abramovsky *et al.* 1976). The mercury vapors are removed from the troposphere through their entrapment by the aerosol particles which take, on the average, 5 days to precipitate. According to Abramovsky *et al.* (1976), the equilibrium between the free mercury and its aerosol-bound forms is reached also within 5 days. Therefore, the life time for mercury in the system "land surface-troposphere" is about 10 days.

The concentration of aerosol-bound mercury having been accepted as equal to the mercury vapor concentration, that is, $0.4\text{-}1.0 \cdot 10^{-9}$ g/m^3, one obtains a rough estimate for the total amount of mercury contained in an air column 1 km high projected onto an area of 1 km^2 as $2 \times (0.4 - 1) \cdot 10^{-9}$ g/m^3 $\times$ 10^9 m^3 = 0.8 to 2 g.

The troposphere contains 100 to 250 tons of mercury over the whole terrestrial surface, except glaciated and desert areas. The air-borne mercury over the oceans having been taken into account, the total of this metal in the Earth's atmosphere is about 300-350 tons.

Having agreed with the above authors that the tropospheric lifetime for mercury is indeed 10 days (which is the period needed for the total of mercury air-borne over the World's land at a particular point in time to precipitate), one arrives at a conclusion that the mercury cycle is repeated 36 times during one year. A point to be noted is that the river and stream loss of this metal amounts to some 2.6 thousand tons per year, that is, about 7.1 ton/day. Most of the metal evaporates and enters the troposphere. Simultaneously, the permanent evaporation of mercury from the ocean surface and its transport to

Table 3.5. Enrichment Factors of Certain Elements in Aerosols in the Vicinity of Active Volcanos (after Boutron 1979)

Element	Relative enrichment factor of volcanic aerosols	
	Kilauea	Etna
Al	1	1
Fe	2.9	0.7
Mn	2.5	5.9
Pb	100	390
Cu	100	240
Zn	140	580
Cd	320	1900
Hg	310000	13000

the land compensate in part for the stream loss and maintain the migration mercury cycle "land surface-atmosphere-land surface". Besides, included in the overall migration is mercury from the Earth's interior, about 1 thousand tons per year (Beus *et al.* 1976), and mercury from industrial atmospheric effluents, in a slightly larger amount. Presumably, the same order of magnitude is the amount of mercury precipitated over the ocean in suspension.

The above estimates are unquestionably very approximate and should not be accepted at face value; nonetheless, it is felt that basically they give a realistic picture of the global mercury transport.

Thus, it may be taken for a well-established fact that the tropospheric aerosols become enriched in definite chemical elements occurring in the gaseous state. It should be noted that the identification of sources responsible for the supply of gaseous heavy metals and their congeners of variable valency represents an arduous task.

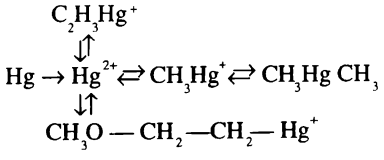
Active volcanos are apparent sources whose actual number on the land is estimated to be about 850. During a period of one year, they eject about $2\text{-}3 \cdot 10^9$ tons of pyroclastic material. Of this, the gas mass accounts, according to Lisitsyn (1978), for 3%, that is, $90 \cdot 10^6$ ton/year. The composition of volcanic pyroclastic material is close to the average andesite composition, that is, with the concentration of heavy metals slightly higher as compared to the granitic layer of the continental Earth's crust. However, the metal concentration in volcanic aerosols tends to increase appreciably. Analyses of aerosols in an immediate vicinity of the volcanos in Sicily, the Hawaiian Islands, and Kamchatka have shown the aerosols to be significantly enriched in heavy metals (Miklishansky *et al.* 1979; Buat-Menard *et al.* 1978). Boutron (1978) has

examined the data of various authors and shown the volcanic aerosols to be 100 and 1000 times higher in heavy metals (relative to aluminum) than the Earth's crust (see Table 3.5). Presumably, this is due to the entrapment by aerosol particles of metals, ejected in a gaseous state from volcanos.

Still, the estimations made have shown that the volcanic activity in itself is not the major factor that might have explained the occurrence *in toto* of heavy metals dispersed in the troposphere. Buat-Menard and Arnold (1978) have measured the annual metal emission from one of the most powerful world's volcanos, Etna. According to the findings by these authors, Etna supplies annually to the atmosphere: copper, 365 tons; lead, 130 tons; zinc, 1100 tons; and cadmium, 10 tons. In the opinion of Boutron, in order to provide for the geochemical background of the troposphere in the northern hemisphere alone, the activity of more than 100 volcanos such as Etna would be required, which is in sharp contrast with reality.

Presumably, along with the volcanism, there must be other sources for the atmospheric supply of gaseous metals. The available evidence indicates that a much more powerful, although less spectacular, factor is the activity of microorganisms and higher plants.

In retrospect of the mercury exchange between land surface and atmosphere, it is to be noted that mercury, despite its easy vaporability, is to a significant extent involved in the atmospheric migration in the form of organometallic compounds which are produced in the course of microbiologic processes. The transformation of metallic mercury into organometallic compounds is actively carried out in aqueous and subaqueous landscapes. In an aqueous medium rich in soluble organic compounds and containing a free oxygen, a series of biogeochemical conversions takes place according to the general scheme shown below (Akopov *et al.* 1976):



Of more common occurrence is the transformation of mercury compounds that proceeds under the conditions of oxygen deficiency via a series of anaerobic microbiological processes leading to the formation of mercury methyl: $Hg^{2+} \rightarrow CH_3Hg^+$, which then converts to mercury dimethyl, $(CH_3)_2Hg$. Mercury dimethyl is a sparingly soluble, but easily vaporable compound. It actively spreads into the atmosphere where, exposed to various kinds of radiation, it reconverts to mercury methyl to be entrapped by aerosols.

Microbiological methylation processes and the formation of volatile organic species involve also most heavy metals incapable, unlike mercury, of evaporation. Wood (1974) was one of the first to point out the importance of the biogeochemical migration cycles of heavy metals and their congeneric elements for the environment.

Biogeochemical mobilization of metals and their involvement in the atmospheric migration are not the only domains of activity for microorganisms and simplest photosynthetic bacteria. The condensed transpiratory vapors of higher plants have been found to contain not only the salts of alkali and alkaline earth elements, but also volatile organic metal complexes. According to Bondarev (1981), the water, transpired by plants, has a mineralization of 40 mg/l, and the terrestrial vegetation carries over into the atmosphere by transpiration a total of $1.2\text{-}1.4 \cdot 10^9$ tons of mineral compounds. The plants exude a vast variety of gaseous species, at an estimated rate of $1.5 \cdot 10^9$ tons per year (Isidorov 1985). The formation of terpenes is typical of coniferous trees, and isoprenes, of deciduous trees. Bondarev (1981) has observed that the daily production of volatile species by the deciduous forest from an area of 1 ha is about 2 kg, and that by the coniferous forest, 4 to 30 kg, which implies the eventual release into the troposphere of as much as $0.5 \cdot 10^9$ tons of volatile organic compounds per year containing $4\text{-}5 \cdot 10^3$ tons of mineral materials.

The studies carried out by Curtin *et al.* (1974) in the mountainous areas of Colorado and Idaho (USA) have shown that the coniferous trees release actively into the atmosphere the cationic elements of inorganic salts (sodium, magnesium, strontium) and numerous metals. Noteworthy, the concentrations of copper, tin, molybdenum, nickel and a number of other elements in the transpiratory condensate ash were higher than those in the needle ash. Simultaneously, different tree species exhibited specific biogeochemical features. In particular, the exudates of the fir *Pseudotsuga menziesii* were found to contain more zinc and less cadmium than those of the spruce *Picea engelmanii* and pine *Pinus contorta*, the exudates of fir and pine contained more strontium than those of spruce, and so forth. Curtin and coworkers believe that the metals are removed from the green organs of trees in the form of volatile complexes with terpenes, isoprene, pinene, and other related species.

Beafort *et al.* (1975) have shown that a leaf area of 1 cm^2 can exude zinc at a rate of up to $1 \cdot 10^{-6}$ μg/h and lead at a rate smaller by a factor of 100. These authors believe that, in global terms, this corresponds to the release of 9 kg of zinc and 5 g of lead from a 1 km^2 vegetation area per year. Based on these data, Lentzi and MacKenzy (1979) have estimated the global supply of zinc by the terrestrial higher plants to the atmosphere as equal to $300 \cdot 10^3$ ton/year. Bondarev (1981) turned attention to the fact that a specific migratory flow could be produced by the dispersal of pollen. A single birch, oak, or spruce tree produces more than $100 \cdot 10^6$ pollen grains per year, whereas with pine, it is

more than $350 \cdot 10^6$ pollen grains per year. The average rate for the production of pollen is 15 ton/km^2·year^{-1}, and the overall pollen production by the terrestrial vegetation is about $1.6 \cdot 10^9$ tons per year. The pollen ash content being 5%, the supply of mineral compounds to the troposphere by pollen dispersal is about $80 \cdot 10^6$ tons.

The pollen and wind-borne vegetable detritus reflect compositionally the elevated metal concentration in the local soils. This effect was used in developing the atmobiogeochemical method of prospecting for sulfide ore deposits in Quebec (Canada) and Arizona (USA) (Barringer 1977; Brooks 1983).

Finally, an important source of the metal supply to the atmosphere are forest fires. The forest fires, viewed on a planetary scale, compare to such catastrophic events as volcanic eruptions, whereas their geochemical consequences may happen to be even more far-reaching. The available estimates show that globally the forest fires emit into the atmosphere $100\text{-}200 \cdot 10^6$ tons of aerosol particles per year. According to Ostromogil'sky *et al.* (1981), the annual emission of metals into the atmosphere is: iron, 350 000 tons; zinc, 250 000 tons; copper, 35 000 tons; lead, 6 700 tons. Probably, these values are slightly overestimated and include metal amounts contributed by low-temperature biological processes; still, there is little doubt that the occurrence of large amounts of metals in the atmosphere should be attributed to forest fires.

Boutron (1978), on the basis of his detailed analysis of the aerosol geochemistry has arrived at a conclusion that, compositionally, three groups of chemical elements should be distinguished in aerosols.

The first group includes the elements constitutive of sea salt which act as condensation nuclei for oceanic aerosols. These elements are sodium (the most typical species), then magnesium, calcium, potassium, strontium, chlorine, and sulfate sulfur. The elemental proportions (relative to Na) within this group are the same both for aerosols and oceanic water.

The second group is represented by aluminum, iron, scandium, yttrium, zirconium, manganese, vanadium, and some others. The proportion of these elements in aerosols (relative to aluminum) is close to the elemental proportions found for the Earth's crust. Obviously, the carriers for these elements are finely dispersed fragments of loose products of weathering of the continental crustal rocks. For this reason, Boutron (1978) named this group as composed of continental detrital elements.

The third group is made up of heavy elements (mercury, lead, zinc, copper, cadmium) and their congeneric elements of variable valency (arsenic, antimony, bismuth). Most of these elements enter the atmosphere as gases. For this reason, they are easily entrapped by condensation nuclei, which makes the aerosol particles enriched (relative to Al) in these elements by 1-2 orders of magnitude vis–à-vis the Earth's crust.

The available evidence has led to infer that the differentiation of chemical elements in the system "land surface-atmosphere-ocean surface" is a result of the long-lasted activity of living matter, and the actual dynamics of cyclic mass exchange involving the third-group elements is mainly due to the recent biogeochemical processes.

3.3. Wash-out and Transfer of Water-Soluble Forms of Chemical Elements in Troposphere

The dust particles, once in the troposphere, act as condensation nuclei and become exposed to multiple contacts (on the average, 10 times per residence time) with condensed water and dissolved therein chloride and sulfate ions. Under such circumstances, a significant part of trace elements pass into a state enabling their solubilization.

One liter of atmospheric water, when dispersed into droplets of medium size, expands on its descent to a distance of 1 km within a volume of about 300 m^3; with finely dispersed droplets, the expansion volume can be much larger. In the process, part of the elements entrapped in the aerosol particles become dissolved. The ratio of soluble-to-insoluble forms of trace elements in the troposphere is subject to large variation and appears to depend on many factors. An analysis of this ratio has enabled one to reach a conclusion that, in the atmospheric suspensoids over the continents, about 50% (by weight) of trace elements persist in a water-soluble state, and 50%, in water-insoluble forms (Miklishansky *et al.* 1978). This conclusion has been confirmed by the observations of trace elements precipitated from the atmosphere onto the land surface. At least 50% of precipitated atmospheric metals reach the ground in a water-soluble form (Zhigalovskaya *et al.* 1974). It stands to reason that each element behaves in a specific manner: for example, copper occurs for the most part in a water-soluble form (80% by weight), whereas with lead insoluble forms (60% or more) are more typical.

One may form an idea of the mass exchange of chemical elements between the atmosphere, World's land, and World's ocean via writing a mass balance on soluble materials that migrate with atmospheric precipitations and river streams. Attempts have been made to take a global balance on the soluble materials (Garrels and MacKenzie 1971; Biogeochemistry of the Ocean 1983; Dobrovolsky 1983; Bezborodov and Eremeyev 1984, to cite a few). All the estimations made were based on the annual water balance, the average stream flow having been taken equal to $35\text{-}37 \cdot 10^3$ km^3. In 1986, updated data were published, which has necessitated a revision of the earlier calculations. According to new data by L'vovich (1986), over $525 \cdot 10^{12}$ m^3 of water is involved

in the global annual water cycle. $456 \cdot 10^{12}$ m^3 of water is evaporated from the ocean surface; of this, most ($412 \cdot 10^{12}$ m^3) is returned to the ocean as precipitation, and $44 \cdot 10^{12}$ m^3 is air-borne onto the land.

About $69 \cdot 10^{12}$ m^3 is evaporated from the land surface. About 20% of the World's land area has no runoff access to the ocean. In this area, the annual amount of precipitations corresponds to the respective amount of evaporated water ($7.5 \cdot 10^{12}$ m^3). On most of the land of area $128 \cdot 10^6$ km^2, the evaporated water is $62 \cdot 10^{12}$ m^3, whereas the precipitations amount to $106 \cdot 10^{12}$ m^3. The difference of $44 \cdot 10^{12}$ m^3 is annually supplied to the ocean as stream flow (included $3 \cdot 10^{12}$ m^3 of glacier flow in the Antarctic Continent and Greenland).

The moving water masses carry an appreciable amount of soluble materials. Various authors have estimated the average supraoceanic mineralization of precipitation to range within 10-20 mg/l. Accepting 10 mg/l as the most probable value, one may presume that $4.6 \cdot 10^9$ tons of salts at least is transferred from the ocean surface into the atmosphere. The average supraterrestrial mineralization of precipitation is 25 mg/l. Therefore, $1.73 \cdot 10^6$ tons of salts is carried over from the World's land surface into the atmosphere to fall finally out as precipitations. A certain amount of salts is known to fall out of the atmosphere in the form of the so-called "dry precipitations" which account for about 20% of the total mass of precipitated salts. With allowance made for the "dry precipitations", the annual supply to the atmosphere from the World's land surface is $(1.73 + 0.35) \cdot 10^9$ tons of salts, and from the ocean surface, $(4.6 + 0.92) \cdot 10^9$ tons. The total mass of salts involved in the water cycle in the World's land terrains with no runoff access is $0.23 \cdot 10^9$ tons (with allowance made for 20% of "dry precipitations").

Table 3.6. Atmospheric Transport of Major Ions from the World's Ocean onto Land

Ions	Supply of ions to land, 1.106 ton/year		Fraction of ions of oceanic origin relative to the mass of continental runoff, %	
	in oceanic precipitation	20% of dry precipitation included	20% excluded	20% included
Na^+	107.1	128.1	54.0	64.7
K^+	7.1	8.6	10.8	13.0
Mg^{2+}	20.9	25.0	14.4	17.2
Ca^{2+}	22.0	26.4	3.6	4.3
Cl^-	200.0	240.3	70.9	85.2
SO_4^{2+}	74.2	82.1	14.1	16.9
HCO_3^-	8.8	10.5	0.3	0.4

Table 3.7. Sea Water Ions Supplied to the USSR Territory from the Ocean via Atmosphere (after Savenko 1976)

Ions	Average composition of precipitation over ocean		Supply from ocean, 10^6 ton/year	Stream loss, 10^6 ton/year	Fraction of ions of oceanic origin in stream loss, %
	mg/l	%			
Na^+	2.24	24.74	19.4	32.0	60.3
K^+	0.12	1.33	1.0	4.6	21.8
Mg^{2+}	0.33	3.66	2.8	18.4	15.5
Ca^{2+}	0.36	3.98	3.1	79.2	3.9
Cl^-	4.00	44.19	34.4	41.1	83.7
SO_4^{2-}	1.64	18.12	14.1	76.6	19.7
HCO_3^-	0.36	3.98	3.1	254.1	1.2
Total	9.05	100.0	77.8	501.0	—

The amount of salts as carried over from the Earth's water surface onto the land ("dry precipitations" included) is estimated to be no less than $0.53 \cdot 10^9$ tons per year. The aerial transport of sea salt is mostly confined to river-drained terrains of the land and is in part counterbalanced by the stream loss of soluble compounds from these terrains.

According to the estimates of Livingston (1963) based on the average mineralization of river waters, the overall terrestrial loss of salts (except the glaciers of the Antarctic Continent and Greenland) amounts to $4.9 \cdot 10^9$ tons. Consequently, about 10% of the salt mass lost from the land into ocean is annually returned from the ocean onto land via atmosphere. The global water cycle is accompanied by a cycling of large masses of salts and chemical elements released into the atmosphere owing to biogeochemical processes.

The reverse migration of water-soluble species does by no means imply that the chemical elements, lost into the ocean, are returned to the land in unchanged proportions. As has been shown in the foregoing subsection, the composition of river waters undergoes a drastic change on transport into the ocean. For this reason, the elemental proportion of dissolved materials in oceanic layers is different from that of river waters. Besides, the elemental proportions are subject to alteration during the formation of oceanic aerosols and the carry-over of chemical elements from ocean to atmosphere. The chemical composition of precipitated atmospheric salts and sea water salts is either not the same.

Now, knowing the concentration of chemical elements in oceanic precipitations and in continental runoff, we can determine the contribution of oceanic elements to the overall amount of elements as returned from ocean onto land (Table 3.6).

Table 3.8. Trace Element Concentrations in Continental Precipitation (after Ostromogil'sky *et al.* 1981)

Element	Concentration range, μg/l	Element	Concentration range, μg/l
Fe	16-4020	As	0.2-31
Ti	3-220	Sb	0.3-4.6
Zn	10-260	Cd	0.05-17.7
Br	0.8-460	V	3.7-9.0
Cu	0.5-82	Mn	1.7-7.7
Pb	0.3-53	Ni	1.0-7.2
Co	0.04-7.2	Hg	0.01-1.3
Se	0.2-0.91		

Since not all details of the water balance are well understood, one must admit that discrepancies in the estimates by various researchers are unavoidable. Nonetheless, the orders of magnitude compare quite satisfactorily. More reliable estimates have been obtained for the territory of the USSR, for which the water balance is known in more details than for the Earth *in toto* (see Table 3.7).

It will be observed in Table 3.6 and 3.7 that a significant part of chloride and sodium ions found in the stream flow has been supplied in the atmospheric precipitation of oceanic origin. The situation with calcium is quite different. Enormous masses of this element are carried over in river streams to the World's ocean to remain there in a bound state. Sulfate sulfur, magnesium, and potassium are less constrained in this process. Most of them is accumulated in the ocean; however, 10-20% of their stream loss becomes involved in the cyclic atmospheric migration between ocean and continents.

The distribution of water-soluble forms of heavy metals and other trace elements appears to be more complex. The data on chemical element concentration in the continental rain water show a large scatter in values (Table 3.8). It is not surprising therefore that the estimates and conclusions of various authors do not always agree. Apparently, the elucidation of these controversial issues requires further studies.

The cyclic processes of mass exchange between the land surface and the troposphere on the one hand, and between the ocean surface and the troposphere, on the other hand, are interrelated. According to our estimates, the overall uptake of disperse soil particles from the World's land surface and their carry-over into the atmosphere amounts to about $5.2 \cdot 10^9$ tons per year. Of this, about $3.5 \cdot 10^9$ tons is returned to the land surface, and $1.7\text{-}1.8 \cdot 10^9$ tons is taken up by the ocean. In the circumcontinental zone around the land periphery, roughly corresponding to the shelf belt, the dust is precipitated at an average rate of

15 g/m^2·year^{-1}. Over open ocean and over glaciated land, the average precipitation rate is appreciably smaller, 3 g/m^2·year^{-1}. Accordingly, in the circumcontinental zone that takes about 10% of the overall Earth's water surface, the dust fall-out is 0.5-0.6·10^9 ton/year, and in the open ocean and glaciated areas, it is 1.1-1.2·10^9 ton/year. In parallel to the dust carry-over, tens and hundreds of thousand tons of zinc, lead, copper and other heavy metals are removed from the World's land.

Simultaneously with the above processes, the opposing flux of heavy metals is directed from ocean to land via the troposphere. Metallization and other biogeochemical processes that favour the formation of volatile metal compounds in hydromorphic terrestrial landscapes are also of wide occurrence in the near-surface oceanic layer. The estimated metal balance for a global "atmosphere-ocean surface-benthic deposits" system has shown that only part of heavy metals precipitated onto the ocean surface from the atmosphere are lost into benthic deposits. Since the metal concentration in oceanic water is maintained constant, it is to be inferred that a significant part of precipitated metals are returned back into the troposphere.

The mechanism of this mass exchange is still unclear in many details, but there is little doubt that the biological processes for formation of volatile organometallic compounds, and primarily methylation, play an important role therein. There are good reasons to presume that the annual transport from ocean to atmosphere involves hundreds of thousand tons of zinc, lead, copper, and other chemical elements which are again returned into ocean with liquid and solid precipitations.

Compositional distinctions between the air-borne aerosols and vapors of continental and oceanic origin clearly manifest themselves as the World's land and World's ocean come in contact with each other. The terrestrial effect most notably shows up in the delivery of finely divided mineral materials into the ocean. In the littoral oceanic zone, the mass of precipitated aerosols is five times that in the pelagic regions of the ocean, and these continental aerosols exhibit higher concentrations of iron, aluminum, manganese, gallium, and other terrigenic trace elements. Consequently, in the littoral zone, the annual surface density of atmospheric precipitation is 0.7 g/m^2 for iron, 20 mg/m^2 for manganese, and 0.9 mg/m^2 for gallium, whereas in the pelagic regions of the ocean, the respective values are 0.09 g/m^2, 1.6 mg/m^2, and 0.06 mg/m^2.

The oceanic influence is also manifest in the supply of water-soluble forms of chemical elements to the coastal strip, particularly, to that of an island. The precipitations of oceanic origin carry in large masses of the major sea salt components (sodium, magnesium, chlorine, sulfate sulfur) increasing thereby the environmental contents of these elements in the near-shore zone. An essential point is that in the precipitations of oceanic origin, the heavy metals and related elements are found in proportions different from those on land.

As has been ascertained, the enrichment factor for the precipitated heavy elements (relative to aluminum or iron) in the coastal strip is higher over that in the interior parts of continents. The sphere of oceanic geochemical influence extends to 100-200 km of the land interior; most commonly, it is confined to even more narrow strips. In geophysical maps, this zone is clearly distinguished by the elevated concentration of thalassophilic elements in the precipitations.

Given the annual amount of precipitation and the concentration of elements, one can estimate the surface density for precipitated salts. According to the earliest estimates by F. Clarke, the World's land surface receives annually 1.8 billion tons of salts through precipitation. A close value has been obtained by us: 1.8 billion tons of salts of continental and 0.44 billion tons of salts of oceanic origin, totalling 2.3 billion tons. This is equivalent to a surface density of about 15 ton/km^2. According to the estimation by Berland (1975), the annual supply of mineral materials in various parts of the Soviet Union (urban areas excluded) through precipitation was 5 to 15 ton/km^2. Zverev and Rubeikin (1973) have evaluated that the precipitation over the entire territory of the USSR supplies a total of 259 million tons of salts per year, which is equivalent to a surface density of about 12 ton/km^2. The mean values for the atmospheric supply of salts are: forest landscapes, 7-11 ton/km^2; steppe landscape, to 17-18 ton/km^2; arid landscapes, to 22 ton/km^2. To be noted is the high supply of salts in littoral regions where, according to the data by an American geophysicist Cadle (1976), it can reach 340 and even 470 ton/km^2 per year. The above data thus provide evidence that the atmospheric migration and material exchange between land, ocean, and atmosphere are important factors contributing to the geochemical nonuniformity of the land surface.

This nonuniformity becomes still more apparent when, after having considered the distribution of the sum total of salts, we turn our attention to the distribution of individual elements. As has been noted earlier, the most active ocean-to-land migrant among the major sea salt ions is chloride and the least active, calcium. For this reason, in the European part of the USSR, the largest precipitations of chloride, demarcated by a 10 kg/ha isoline (or 1 ton/km^2) are confined to coastal strips in the north and the south, whereas the smallest precipitations are recorded in the interior continental regions (Fig. 9). Entirely unlike distribution is observed for calcium as supplied in atmospheric precipitations. Most of this element falls out over the territory of the Ukraine (more than 30 kg/ha); northward, the fall-out surface density for calcium tends to decrease reaching 8-16 kg/ha in the central regions of the European part of the USSR and 3 kg/ha in the northern regions.

Nonuniform fall-out distributions over the land surface have also been recorded for trace elements. In aerosols, the relative concentrations of certain trace metals (copper, nickel, cadmium) with respect to iron tend to increase on passing from the intracontinental to the coastal territories and further to

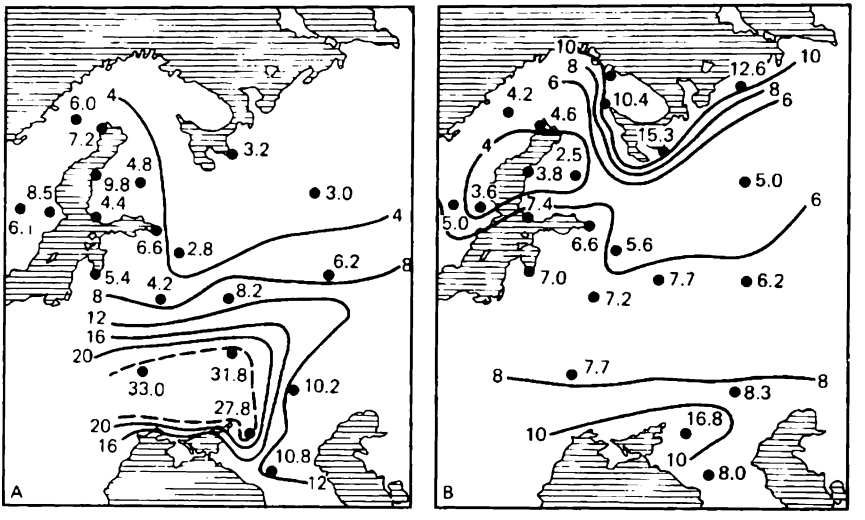


Fig. 9. Annual fallout of calcium (A) and chlorine (B) supplied to the soil in atmospheric precipitation (kg/ha)

the open ocean (Dobrovolsky 1980). Thus, the intrinsic geochemical nonuniformity of the lithosphere does not become levelled-off on the land surface, but rather becomes more contrasted owing to the atmospheric migration of chemical elements.

It is noteworthy that the atmospheric precipitation of chemical elements does not lead to their ever-increasing accumulation in the land *in toto* or in its separate areas. This fact is explained by the cyclicity of mass exchange in the systems "land–atmosphere–land" and "land–ocean–atmosphere–land". To a first approximation, in the planetary aspect, a definite excess of the continental stream loss over the supply of oceanic salts to the land provides for the ocean's dynamic equilibrium, the material exchange within the "ocean–atmosphere–ocean" system, and the formation of sedimentary deposits. To a second approximation, under more detailed analysis it becomes apparent that the global migration cycles include less extended cycles confined to specific territories.

Various territories are characterized by different masses of chemical elements involved in cyclic-water and atmospheric migrations. For example, in the littoral territories which are recipients of larger amounts of oceanic salts, the respective masses of these salts become involved in the water migration and enter the cycle of "land–ocean–atmosphere–land" system. The migratory elements pass the littoral territory in transit, and are merely in part retained in its small areas. Intracontinental territories, responsive to the oceanic air currents, receive small amounts of salts through precipitation; accordingly, small masses of salts

become involved in water migration. To further exemplify, one may refer once again to intracontinental arid regions which receive large amounts of salts via atmospheric precipitation. This may give rise to an impression that such a regime would favour progressive salinization. In reality, roughly the same amount of salts is entrained by wind to enter the cyclic "land–atmosphere–land" migration. In particular, such situations are typical of Kazakhstan and the Central Asia, where the atmospheric precipitation supplies salts at an average rate of about 20 ton/km^2·year^{-1}, which is twice as large compared to the norms in forest-steppe and south-taiga areas of Western Siberia. A study of the movement of dust masses over the plains of the Central Asia and Kazakhstan has shown that the bulk of dust circulates within the confines of these regions. Presumably, the same holds for air-borne salts also.

3.4. Composition of Terrestrial Surface Waters in Relation to Biogeochemical Processes

Living matter of the Earth is inalienably linked to liquid water. Water is conditio sine qua non for the existence of living matter. Water accounts compositionally for 60% of the total mass of terrestrial living organisms and for 80% of the mass of oceanic organisms. All physiological processes and biochemical reactions proceed in aqueous media. Enormous amounts of water undergo decomposition during photosynthesis. The interaction between living matter and hydrosphere is one of the global processes occurring in the biosphere.

The major part of the Earth's water shell is formed by the World's ocean, with its capacity about $1370 \cdot 10^6$ km^3. The ocean is continuously replenished by run-off waters from the land at a rate of about $44 \cdot 10^3$ km^3/year, according to the recent data of Gol'dovich (1981).* Therefore, the total amount of water available in the ocean at a particular point in time will be completely renewed within a period of about 35 thousand years. The dynamic constancy of the ocean capacity is maintained through evaporation of water at a rate of $44 \cdot 10^3$ km^3/year and its transport in the vapor state followed by precipitation over the land.

The chemical composition of the precipitation, once in contact with the vegetation and the soil, undergoes alteration by the action of humic acids, higher plant metabolites, and soil microorganisms. Carbon dioxide, the end product of organic matter breakdown, is readily soluble in water to yield carbonic acid.

* This value includes the overall stream flow proper ($39 \cdot 10^3$ km^3/year), annual flow from the glaciers of Antarctica and Greenland ($3 \cdot 10^3$ km^3 /year), and subterranian flow from the land ($2 \cdot 10^3$ km^3/year).

Table 3.9. Forms of Occurrence for Heavy Metals in the Amu Darya Water (after Kulmatov 1988)

Form of occurrence	Metals (% of content)			
	Fe	Cr	Co	Zn
Suspended particles > 0.85 μm	8.3	1.8	14.0	11.0
Suspended particles 0.12-0.85 μm	0.5	1.1	3.2	1.9
Colloidal particles, positively charged	20.0	5.3	2.8	4.2
Colloidal particles, negatively charged	13.0	2.7	2.3	1.3
Neutral molecules	7.7	8.1	5.9	17.0
Cations	42.0	49.0	23.0	59.0
Anions	7.4	31.0	48.0	4.2
Total	98.9	99.0	99.2	98.6

These are factors contributive to the dissolving ability of surface water with respect to the mineral matter of the Earth's crust. Simultaneously, the run-off land water entrains the particles of mineral matter, transformed through the agency of living organisms, and carries them over as suspensoids. Thus, the composition of both soluble species and finely divided suspensions is affected by biogeochemical processes.

The surface land waters flow down to rivers. The riverine run-off provides for a powerful geochemical flow playing an important role in the planetary mass exchange between the World's land and the ocean. A point to be emphasized is that the mobilization of chemical elements, involved in water migration, is elicited by the activity of living organisms.

In view of the aforementioned, the stream waters should be regarded as composite solutions containing both suspended disperse particles and truly soluble compounds.

The main forms for the occurrence of chemical elements in stream water are:

1. Simple and complex ions.
2. Neutral molecules, mostly ligated to an inorganic complexing ion. The species classifiable into groups (1) and (2) are 1 nm and less in size.
3. Colloidal particles sizing 0.001 to 0.1 μm, with ions taken up at their surface.

4. Finely dispersed particles consisting for the most part of clay minerals and measuring 0.5 to 1-2 μm.

5. Large suspended particles from clastic minerals of 2-3 to 10 μm in size.

In practice, the suspended particles are separated by means of membrane filters with pores of 0.4-0.5 μm. The separation of suspensions of larger size can be effected using centrifugation. The separation of finely-divided particles is a laborious and time-consuming procedure, seldom used in routine analyses.

As an example, given in Table 3.9 is the water composition of the Amu Darya. The water mineralization and the concentration of dispersed material (turbidity) vary from river to river. According to the data of Livingston (1963), we have accepted the average mineral content of the World's rivers to be equal to 120 mg/l. Based on this estimate and the annual stream flow of $44 \cdot 10^{15}$ l/year, the amount of soluble compounds carried in streams off the land is $5.3 \cdot 10^9$ tons per year. According to Lisitsyn et al. (1983), the average concentration of suspended disperse particles in the continental run-off is 500 mg/l. Therefore, the global stream loss of finely-dispersed materials is equal to $22 \cdot 10^9$ ton/year, which is 4.2 times as large as that of soluble compounds.

The weight ratio of soluble compounds and solid suspensions in the river stream is to a significant extent dependent on the nature of land vegetation. The recorded facts provide evidence that in the course of geological history, this ratio was subject to multiple variations. On this basis, the French soil scientist Erhart (1956) has developed a theory of biorhexistasie. The epochs of biostasie (biological equilibrium) were characterized by a wide spread of stable forest phytocenoses which protected the soil from mechanical erosion and facilitated the involvement of chemical elements in water migration in soluble forms. In the epochs of rhexistasie, the biological equilibrium became increasingly impaired owing to the extensive deforestation. As a consequence, the denudation and erosion processes become more active causing the concentrational rise of solid suspensions in the run-off stream.

3.4.1. Soluble Compounds in the River Stream

In the river waters, the most common soluble species are HCO_3^-, SO_4^{2-} and Cl^- anions accounting, respectively, for 48.8%, 10.0% and 5.3% of the sum total of soluble compounds. Among the cations, calcium (10.8%), magnesium (2.7%), sodium (3.7%), and potassium (1.2%) are typical. The rest of the elements are present in variable trace amounts.

Numerous attempts have been made to explain the concentration of minor chemical elements in natural waters within the framework of an ionic theory of solutions, assuming that only one factor (for example, ionic potential, hydrogen ion concentration (pH), or oxidation-reduction potential) was essentially important.

Garrels and MacKenzie (1971) explained the elemental distribution in natural waters using a model "nondiluted solution-precipitate" in their physico-chemical calculations. According to their concept, the occurrence of an element in solution is dependent on the combination of oxidation-reduction and acid-basic conditions which can be depicted in Eh–pH diagrams. For the solution-precipitation processes involving macrocomponents such an approach seems to be quite acceptable, whereas for trace elements it may prove to be at variance with reality. For this reason, when arguing for the applicability of one or another theory to natural aqueous solutions, one must rely on a thorough analysis of the available experimental evidence.

The river waters contain soluble forms of trace elements not involved in the biological cycle. The terrestrial stream waters commonly exhibit the pH value falling into a range of 4.5 to 8.5. Under such pH conditions, many of the metals (zinc, chromium, copper, beryllium, lead, cadmium, nickel, cobalt, and others) may exist in a state of solution, form a precipitate, or pass once again into solution. In reality, the factual concentration of trace elements in natural waters is so insignificant that the variation in pH produces little effect on the state in which trace elements persist. The concentration of metals in pure water is most commonly lower than their level in a solution after hydroxide precipitation. In certain cases, when insoluble metal hydroxides are formed in negligibly small amounts, they tend to form nonprecipitable subcolloidal flocculates and can actively migrate in the state of a dilute colloid solution. Simultaneously, the trace elements present in the solution can be taken up by gels of macroelemental compounds (primarily, by iron hydroxides), finely-dispersed clay particles and even suffer precipitation, in complete disaccord with theory.

A significant part of trace elements occur in natural waters as constituents of complex compounds, rather than simple ions. A trace element, once in a complexed state, exhibits stability in solution over a wider range of conditions as compared to the acid-basic and oxidation-reduction conditions for stability of the simple ion. As shown by Shcherbina (1972), the formation of inorganic complex compounds is typical of chromium, nickel, cobalt, copper, zinc, uranium. Compounds that arise are of the type $[Cu(NH_3)_2]^+$, $[Cu(CO_3)_2]^{2-}$, $[ZnCl_3]^-$, $[Zn(SO_4)_2]^{2-}$, and the like.

Complex organic, especially intracomplex (chelate) compounds play an important role in the aqueous migration of metals. In such compounds, the central metal ion is linked through ionic or coordination bonds with functional groups within the molecule. Most commonly, the ionic bond involves groups COOH, OH, NH_2, SO_3H, OH, and the coordination bond, groups NH_2, NH—N=, =NOH, OH, C=O, S=O, =S—. Amino acids, aromatic compounds (polyphenols), fatty acids, heterocyclic compounds of quinoline type, humic acids and fulvic acids take part as ligands in complexation (Yakushevskaya 1973). The

Table 3.10. Soluble Forms of Chemical Elements in Riverine Waters and Their Involvement in Aqueous Migration

Elements and ions	Average concentration		Global stream loss, 10^3 ton/year	Coefficient of aqueous migration
	in water, g/l	relative to sum total of salts, %		
Cl	6400	5.33	262400	313.0
SO_4^{2-}	12000	10.00	492000	—
S	3960	3.30	162360	82.5
HCO_3^-	58500	48.75	2398500	—
Ca	13000	10.80	533000	4.6
Mg	3300	2.75	135300	2.3
Na	4500	3.75	184500	1.7
K	1500	1.25	61500	—
NO_3	1000	0.83	41000	0.5
N	225	0.19	9225	—
SiO_2	13100	10.9	537100	—
Si	5700	4.78	233700	0.15
Fe	670	0.558	27470	0.15
Al	75	$625 \cdot 10^{-4}$	3075	0.01
Sr	80	$667 \cdot 10^{-4}$	3280	2.90
P	20	$167 \cdot 10^{-4}$	820	0.21
F	40	$333 \cdot 10^{-4}$	1640	0.46
Ba	25	$208 \cdot 20^{-4}$	1025	0.31
Br	20	$167 \cdot 10^{-4}$	820	76.0
Zn	20	$167 \cdot 10^{-4}$	820	3.27
B	18	$150 \cdot 10^{-4}$	738	15.0
Mn	10	$83 \cdot 10^{-4}$	410	0.12
Cu	7	$58.0 \cdot 10^{-4}$	287	2.64
Ti	4	$33.0 \cdot 10^{-4}$	164	0.01
I	3	$25.0 \cdot 10^{-4}$	123	50.0
Zr	2.5	$21.0 \cdot 10^{-4}$	103	0.12
As	2	$17.0 \cdot 10^{-4}$	82	8.95
Ni	2.5	$21.0 \cdot 10^{-4}$	123	0.81
Li	2.2	$18.0 \cdot 10^{-4}$	90	0.08
Rb	1.8	$15.0 \cdot 10^{-4}$	74	0.08
Cr	1	$8.3 \cdot 10^{-4}$	41	0.24
Mo	0.9	$7.5 \cdot 10^{-4}$	37	5.77
Pb	1	$8.3 \cdot 10^{-4}$	41	0.52
Sb	0.9	$7.5 \cdot 10^{-4}$	37	37.5
Sn	0.5	$4.2 \cdot 10^{-4}$	21	1.56
U	0.3	$2.5 \cdot 10^{-4}$	12	0.96
Co	0.25	$2.1 \cdot 10^{-4}$	10	0.29

Table 3.10 *(continued)*

Elements and ions	Average concentration		Global stream loss, 10^3 ton/year	Coefficient of aqueous migration
	in water, g/l	relative to sum total of salts, %		
Ag	0.2	$1.7 \cdot 10^{-4}$	8.2	35.42
Cd	0.2	$1.7 \cdot 10^{-4}$	8.2	10.63
Ga	0.09	$0.75 \cdot 10^{-4}$	3.7	0.04
Hg	0.07	$0.58 \cdot 10^{-4}$	2.9	17.58
Th	0.05	$0.42 \cdot 10^{-4}$	2.1	0.03
Sc	0.02	$0.17 \cdot 10^{-4}$	0.8	0.02

stability of a complex is dependent on the polarizability of both the complexing cation and organic ligand, the pH, and the trace metal concentration. Most commonly, the complexes are stable in weakly acidic and neutral waters, and tend to dissociate with increasing pH. Interestingly, the highest stability of chelate compounds is attained at a low metal concentration, whereas with the metal concentration increasing, the complexes tend to break down.

Organometallic complex compounds are of very wide occurrence. On the territory of forest landscapes with acid soils, these compounds represent the predominant form for dissolved metals. As aridity increases in parallel with the pH rise of soil solutions and surface waters, the role of complexes as metal carriers becomes less conspicuous retaining, however, sufficient importance. For example, in the water of the Dnieper, more than half of dissolved metals persist in the form of organometallic compounds.

The diversity of the forms of dissolved elements, provincial geochemical and bioclimatic distinctions of the catchment areas are factors responsible for large compositional variations of stream waters. For this reason, the determination of the average concentration of elements in the terrestrial waters is inherently more arbitrary as compared to the oceanic water. In our calculations, summarized in Table 3.10, we have used the data which we believe to be the most reliable (Vinogradov 1967; Lisitsyn 1978; Goldberg 1965; Bowen 1966; Turekian 1969).

Although the overall mineral content of fresh waters is much less than that of saline sea waters, the global stream loss of dissolved trace elements is quite significant. For fluorine, strontium, iron, aluminum, the annual stream loss amounts to millions of tons; for calcium, sodium, magnesium, sulfate sulfur,

chlorine, silicon, hundreds of millions of tons; for potassium, tens of millions of tons; for bromine, iodine, boron, also for zinc, manganese, and copper, hundreds of thousands of tons. Most trace elements are removed from the land in the annual amount of tens of thousand tons. Only a small number of elements are lost in lesser amounts.

3.4.2. Intensity of Aqueous Migration of Chemical Elements

The concept of the stream loss of dissolved masses of elements will be incomplete unless supplemented with a quantitative estimation of the elemental involvement in the aqueous migration. Polynov (1933) has shown that the intensity of aqueous migration of an element is determined not by the element's concentration in water, but rather by the ratio of this concentration to the concentration of the element in the rock from which the element is drained off.

Perel'man (1975) proposed the use of a factor known as the coefficient of aqueous migration (K_w) which is defined as the ratio of the concentration of the element in the dry residue of a water sample to the concentration of the element in the rock. In estimating the extent of involvement of an element in aqueous migration on a global scale, one must know the ratio of the average content of the element in the dry residue of stream water to the abundance of the element in the continental granitic layer.

In terms of the K_w coefficient, the extent of involvement of the elements in aqueous migration is characterized in the following order:

$K_w = 100n$: Cl;
$K_w = 10n$: N, S, I, Br, Ag, Sb, Hg, Se, Cd;
$K_w = n$: As, B, Mo, Ca, Zn, Sr, Cu, Mg, Na, Sn, F;
$K_w = 0.1n$: U, P, Ni, Li, Pb, K, Co, Ba, Cr, Y, Si, Mn, V, Zr;
$K_w = 0.01n$: Rb, Th, Ga, Sc, Ti.

3.4.3. Migration of Elements Suspended in Stream Flow

All the facts and conclusions that have been considered earlier bear relevance to the elements in a state of solution. Completely different relationships are found for the chemical elements and their masses that migrate as suspensions in stream flows. Major reasons of this are, first, that the mass of suspensions in the annual stream loss is four times the mass of soluble compounds; second, compositionally the stream suspensions exhibit specific features.

Table 3.11. Stream Loss of Chemical Elements Transported in Suspended State by Rivers

Elements	Concentration, $g \cdot l^{-1}$ (Gordeyev 1983)	Annual stream loss of suspended forms of elements, 10^3 ton·year^{-1}	Sum total of dissolved and suspended forms, 10^3 ton·year^{-1}	% of suspended forms relative to overall loss
Si	117000	4797000	5030700	95.4
Al	38200	1566200	1569275	99.8
Fe	23500	963000	990970	97.2
Ca	11500	471500	1004500	46.9
K	6900	282900	344400	82.1
Mg	5750	235750	371050	63.5
Na	4600	188600	373100	50.4
Ti	1840	75440	75604	92.8
P	510	20910	21730	96.2
Mn	500	20500	20910	98.0
Ba	280	11480	12505	91.8
Zn	143	5863	6683	87.7
Zr	92	3772	3875	97.3
Sr	69	2829	6109	46.3
Pb	69	2829	2870	98.6
Rb	55	2255	2329	96.8
Cr	60	2460	2501	98.4
Ni	38.6	1583	1705	92.8
Cu	37	1517	1825	83.1
B	32	1312	2050	64.0
Li	14	574	664	86.4

Sc	9.2	377	380	99.2
Co	8.3	340	350	97.1
Ga	8.3	340	344	98.8
Th	4.6	187	189	99.6
As	2.3	94.3	176	53.4
Mo	1.4	57.4	94.0	60.6
Sb	0.9	36.9	74.0	50.0
Ag	0.6	24.6	32.8	75.0
Cd	0.32	13.1	21.9	59.8
U	0.14	57.4	17.7	32.2

The stream suspensions are mostly made up of finely-dispersed clay particles, clastic quartz particles, and flocculated iron hydroxides. Obviously, such elements as silicon, aluminum, and iron must be present in the suspensions in a higher percentage than in the sum total of the soluble species (see Table 3.11); still, the exact opposite holds for calcium. For the majority of elements, their elemental concentration in suspension is appreciably higher than in solution.

Lisitsyn *et al.* (1983) have argued convincingly that the bulk of trace elements lost into stream waters is associated with suspensions. One will observe, in examining the data in Table 3.11, that over 98% of the mass of elements with low coefficients of aqueous migration ($K_w < 0.05$) is carried over in stream suspension: aluminum, titanium, gallium, lead, thorium, scandium; for elements with K_w from 0.05 to 0.9, this makes up to 90-98% of the mass: silicon, iron, manganese, phosphorus, barium, zirconium, rubidium, chromium, cobalt, nickel. Many elements exhibiting a high intensity of aqueous migration at the value of K_w 1 to 10 for the most part migrate in a state other than that of solution. For magnesium, zinc, copper, and molybdenum, some 65-85% of the mass lost into streams from the World's land territory is transported in the forms bound to the suspended particles. The preferably water-soluble state in the stream flow is typical only of a limited number of elements: nitrogen, chlorine, sulfur, calcium, potassium, bromine.

Listed in the second column of Table 3.12 are the average concentrations of certain elements carried over in the stream flow in a suspended state; for comparison, the third column lists the respective elemental concentration in the sum total of the dissolved compounds. As is easily seen, concentration in suspensions is higher for most elements. It is noteworthy that the relative concentration of chemical elements in stream suspension is not coincident with the respective crustal abundance. Therefore, the suspended matter of the stream flow should be regarded not as a mechanically disintegrated crustal material but as a product of transformation of the latter. Given in the third column of Table 3.12 are the value of factor K_s defined as the ratio of the average concentration of an element in stream suspension to its respective abundance in the continental Earth's crust.

In terms of factor K_s, the elements may be classified into three groups. Group 1 includes the elements with the values of K_s less than 1, which implies a lesser content of an element in suspension relative to its crustal abundance. Representatives of this group are calcium, sodium, strontium, barium, and lithium. The concentration of suspensional magnesium with respect to its crustal abundance remains essentially unchanged ($K_s = 1$).

Group 2 is formed by the elements whose K_s is equal to or slightly in excess of 1. These are titanium, zirconium, gallium, also iron and manganese. Group 3 comprises the elements whose concentrations in suspension tends clearly to

Table 3.12. Relative Enrichment of Stream Flow Suspensions in Heavy Metals

Elements	Average concentration in stream flow suspensions (Martin and Meybeck 1979), μg/g	Average concentration in sum total of soluble matter of stream water, μg/g	Factor K_s
Group 1			
Ca	21500	108000.0	0.8
Na	7100	37500.0	0.3
Mg	1050	27500.0	0.98
Sr	150	667.0	0.6
Ba	600	167.0	0.9
Li	25	0.8	0.8
Group 2			
Ti	5600	33.0	1.7
Zr	200	21.0	1.1
Ga	25	0.8	1.3
Fe	48000	5580.0	1.3
Mn	1050	83.0	1.5
Group 3			
Zn	350	167.0	6.9
Pb	150	8.3	9.4
Cu	100	58.0	4.5
V	170	7.5	2.2
Cr	100	8.2	2.9
Ni	90	17.0	3.5
Co	20	2.5	2.7
Cd	10	1.7	6.2

increase, with the K_s falling within a rage of 2 to 9. Heavy metals form this group: lead, zinc, copper, nickel, cobalt, chromium, vanadium, and cadmium.

The clearly visible tendency of heavy metals to accumulate in stream suspensions provides a good reason to presume that this behaviour is associated with biogeochemical processes. Involved in the aqueous migration on land are

chemical elements which do not enter the biological cycle. Possibly, the stream loss of significant masses of heavy metals tightly imbedded in disperse products of weathering and soil formation is one of the mechanisms for protection of the World's land living matter from excess masses of these elements.

3.4.4. Natural Geochemical Anomalies in Surface Waters of the Land

The surface waters as they come in contact with rocks abundant in trace elements become enriched in these elements. This gives rise to natural hydrogeochemical anomalies. The enrichment is especially active when the open and ground waters are in contact with sulfide ores. The oxidation of iron sulfides is accompanied by hydrolysis to sulfates, precipitation of iron hydroxides, and formation of sulfuric acid which enhances the dissolving power of water. Sulfate species that are formed by oxidation of zinc, copper, and nickel sulfides are readily soluble in water, and therefore these metals become actively involved in aqueous migration.

Most of the migratory metals, because of their reactions with other water-soluble compounds and the uptake by suspended particles are relatively quickly removed from solution, their concentration drops down to the level of local geochemical background. For this reason, the natural hydrogeochemical anomalies in stream waters are never extensive and seldom reach beyond a few hundreds of meters.

Much more extensive, reaching several kilometers in distance, are anomalously high concentrations in bottom sediments which are the precipitated particles of aqueous suspensions. The water analysis of small streams and, especially, of their bottom sediments for metal content has been widely used in geochemical prospecting of ore deposits in many regions of the USSR, Canada, USA, Great Britain, Zambia, Uganda, Phillipines, and other countries.

The accumulation of chemical elements in water exerts influence on aquatic biocenoses. Various manifestations of eutrophication in small stagnant or slow-flowing water bodies are of wide occurrence. The metal concentration in floating and underwater plants, the residents of such reservoirs, is most commonly higher than the average values. High natural concentrations of certain elements in open and ground waters lead to elevated levels of these elements in the local vegetation. The use of such vegetation as cattle food may cause diseases in the farm animals. Similar cases were reported in the USA (Ebens *et al.* 1973), Ireland and Great Britain (Webb *et al.*, 1966), and the USSR (Koval'sky 1974).

It should be emphasized, as a final remark, that the natural geochemical anomalies in surface waters of the World's land are very localized and produce no effect on the mass balance of chemical elements in global biogeochemical cycles.

3.4.5. Transformation of Geochemical Composition of River Waters on Their Flowing into the Ocean

The overall stream runoff supplies enormous masses of chemical elements to the ocean. According to the estimates of Lisitsyn *et al.* (1983), the annual stream loss of metals, as suspensions and soluble forms, respectively (in milliontons) is: iron, 945 and 15; manganese, 20.4 and 0.35; zinc, 5.75 and 0.71; copper, 1.48 and 0.25; lead, 2.8 and 0.04; nickel, 1.55 and 0.089; cobalt, 0.33 and 0.011. Of those, over 92% is deposited in the fringing seas, especially at the estuarial areas, and merely 7.8% is carried over to deep-water oceanic regions.

Along with the precipitation of most suspensions and compounds of major chemical elements, also trace elements are precipitated, often to form large deposits. A significant part of ore reserves of manganese, copper, vanadium, and other metals are of sedimentary origin. Still larger amounts of metals are deposited in a dispersed state, in co-precipitation with widespread compounds. For example, the rapid breakdown of organoferric complexes in alkaline sea water and the vigorous precipitation of iron hydroxide flocculates are accompanied by the uptake of scandium, cobalt, nickel, copper, and vanadium. The deposition of phosphates leads to accumulation of a distinct set of coprecipitated trace elements.

Thus, the peripheral zone of the World's ocean serves as a global geochemical trap for most materials carried off the continents. Nonetheless, large masses of trace elements pass through this natural zone and escape into open ocean.

A detailed analysis of geochemistry of the ocean is beyond the scope of this book. This is a large topic and should be treated in a special monograph. Still, in outlining the influence of the ocean on biogeochemical processes that occur on land, the following must be noted.

The geochemical compositional structures of oceanic and continental waters are basically different. In the latter, most trace elements are concentrated in the suspension material, whereas in the ocean the dissolved forms become increasingly more important. In oceanic water, the diversity of suspended forms of elements is incomparably inferior to that of soluble forms. Even elements reluctant to form solutions such as lead, scandium, yttrium, zirconium, titanium, and chromium occur in the ocean mostly in a dissolved state. Besides, compositionally the World's ocean is formed not only under the influence of runoff waters, but also owing to the contributions from the Earth's interior as a result of the volcanic activity and formative processes of the oceanic crust in tectonically active benthic zones.

The compositional comparison of continental and oceanic waters clearly reveals their distinction. The river water contains a thousand times less than chromium, bromine, sodium, a hundred times less than boron, sulfate sulfur,

Table 3.13. Enrichment Factors for Trace Elements in Oceanic and Stream Water (relative to iron content)

Elements	Enrichment factor	
	Oceanic water	Stream water
Br	324000000.0	492.0
B	4670000.0	53.6
I	1340000.0	538.0
Sr	352000.0	18.8
Mo	81700.0	41.7
Li	60200.0	3.6
Hg	48400.0	110.0
Ag	22300.0	346.0
F	19100.0	65.0
Sb	16100.0	250.0
As	14300.0	56.0
U	13500.0	10.0
Cd	7270.0	68.2
Rb	7060.0	0.6
Se	6670.0	76.9
Zn	1050.0	21.4
Cu	426.0	16.4
V	267.0	0.6
Ni	208.0	4.2
Sn	78.7	10.0
Cr	62.8	1.6
Co	44.0	2.2
Pb	20.0	3.4
Mn	6.3	0.8
Y	3.8	1.0
Ti	3.2	0.1
Zr	1.6	0.8
Sc	0.9	0.2
Th	0.3	0.4
Fe	1.0	1.0

magnesium, potassium, and ten times less than strontium, calcium, lithium, rubidium, fluorine, and iodine. Simultaneously, the stream waters carry ten times more manganese, yttrium, lead, thorium, and appreciably more silicon, titanium, zinc, and copper. Thus, the entry of runoff waters into the World's ocean is followed by a substantial redistribution of the dissolved masses of trace elements.

In the course of the above process, the compositional transformation is reflected in both the concentrational and proportional changes of elements. It has been long known that the concentration of many heavy metals is lower in the oceanic than in the riverine water. However, the fact that the decrease in the absolute metal content is concomitant with a drastic change in the metal proportion has for a long time been underestimated. The occurrence of iron in the oceanic water in a concentration nearly 200 times smaller than that in the river water, the respective ratio being merely 7 and 4 for copper and zinc, signifies the relative enrichment of oceanic water in the two last-mentioned metals.

To estimate the change in elemental proportion as a result of the riverine transport of elements to the ocean, the Japanese geochemist Sugawara (1961) suggested the use of an enrichment factor. To determine this factor, (i) the crustal concentration of a given element is divided by the crustal concentration of a reference element; (ii) the aqueous (river or oceanic) concentration of the element is divided by the aqueous concentration of the reference element; (iii) the enrichment factor is obtained through dividing the latter ratio by the former (crustal) ratio. The conventionally accepted reference element in the above estimation is iron.

The data listed in Table 3.13 show that the confluence of continental (riverine) and oceanic waters causes a profound change in the proportion of dissolved elements. The most notable increase in relative concentration is observed for the elements exhibiting a high absolute concentration in the ocean (bromine, boron, iodine, fluorine, strontium, lithium). In molybdenum, mercury, and uranium, the absolute concentration increases merely several times, whereas the relative concentration, a thousand times. In a similar manner, a large increase of the relative concentration is recorded for antimony, silver, cadmium, selenium, and arsenic, although their absolute concentration in the oceanic water is lower than in the riverine, or nearly the same (as for arsenic).

In other trace elements, the relative concentration increases ten and hundred times. It undergoes a small change only in the metals which, similar to iron, show a marked trend to precipitate on exposure to oceanic water, in the peripheral zone of the World's ocean. Such are thorium, scandium, zirconium, titanium, yttrium, and manganese.

In studying the geochemistry of stream waters, a question arises involuntarily as to the sources and routes of supply of chemical elements to the ocean.

The actual composition of the World's ocean is the final stage of a long history. The bulk of sea water salts is represented by chlorides and sulfates of sodium, magnesium, calcium, and potassium. Such a combination of cationic and anionic chemical elements seems to be paradoxical from a geochemical point of view. The crustal content of the former is several percents each, whereas for the latter it is smaller by about a factor of 100: for example, the

abundance of chlorine is $1.7 \cdot 10^{-2}$% and that of sulfur, $4.7 \cdot 10^{-2}$%. Since both the cations and anions are found in sea water in equivalent amounts, they could not be supplied from only one source, in particular, as leacheates from the continental Earth's crust. Calculations have shown that of the whole chlorine currently available in the ocean in an ionic form, only 1/2900th fraction could have been extracted from the Earth's crust. Therefore, the cations and anions as constituents of sea water are of different origin. In addition to chlorine and sulfur, the anionic elements of ocean water include nitrogen, bromine, iodine, boron, arsenic, selenium, molybdenum, and mercury. It has been argued, not without reason, that the supply of the bulk of these elements is linked to the melting-out of the primary Earth's crust and to the mantle degassing.

The hydrosphere-to-Earth's crust mass ratio is close to the relative content of water vapors in basalt outflow. Presumably, the melting-out of the primary basaltic lithosphere was accompanied by the eruption of water vapors which then condensed to form an ancient ocean. Simultaneously, the above-mentioned anionic elements might also be gaseous eruptive products. Subsequently, in the course of weathering and soil formation and by the action of ever-intensifying biogeochemical processes, the cationic elements became subject to leaching out of the continental Earth's crust, which has finally led to the actual equilibrium between anions and cations in the ocean.

4 Biogeochemistry of Pedosphere

4.1. Soil and Pedosphere

Soil is a unique natural system. A major property of the soil is the inalienable interrelation of its constitutive living and non-living components. An artificial separation of the soil components makes the very existence of the soil impossible and destroys it completely as a system. V.I. Vernadsky aptly named the soil a "biolatent body".

The composition of the soil is quite complex. Present in the soil are not only the solid, but also liquid (soil solution) and gaseous (soil air) phases. The solid phase represents a polydisperse system, with relatively large particles sizing over 0.01 mm, and finely-dispersed particles smaller than 1 μm in size. Components of different size are also distinguished in mechanical and physico-chemical properties. The soil consists of both mineral and organic compounds. The mineral part, in turn, is very diversified and is made up of clastic minerals of parent rocks as well as various soil-hypergene formations. A major specific feature of the soil is that it is the habitat for a vast variety of living organisms.

The soil has evolved to function as a system owing to the interrelated and interdependent biotic activity of various groups of organisms. Among these, are distinguished: organisms involved in the photosynthetic production of organic matter (higher plants); organisms aimed at the destruction of annually senescing and decaying plant organs (edaphic mesofauna); organisms whose function is a profound transformation of decay products, down to their complete mineralization attendant by the release of CO_2 and formation of specific organic edaphic species (microorganisms). Not to a lesser extent are components of the non-living part of the soil diversified as represented by various forms of dead organic matter, fragments of durable hypogene minerals and numerous products of soil-hypergene transformation of the parent rocks.

The provision of photosynthetic organisms with elements of soil nutrition is connected with two major soil components. The first of these is the dead organic matter which is a supplier, owing to the incessant biotic activity of mesofauna and microorganisms, of elements assimilable by the photosynthetic bacteria and indispensable for their reproduction. The interaction of photosynthetic bacteria and heterotrophic organisms provides for a cyclic migration of

the elements in the "vegetation-organics" system of the soil. The second component of the soil, a source of accessible forms of chemical elements for higher plants, are mineral disperse particles which, owing to their very large specific area per unit volume contain appreciable amounts of sorbed chemical elements. These elements resist leaching by the rainfall moisture filtering through the soil, but are readily taken up by the plant roots. The finely-dispersed mineral matter plays a pivotal role in the mechanism of the biological elemental cycle.

The soil micromorphology is also an important factor. The aggregation of soil particles facilitates the preservation and regulated supply of water and nutritional elements to higher plants. The system of interaggregate voids and pores favours the free gas exchange between the soil and the lowermost tropospheric layer, and makes easier the release of the gas products of soil formation, primarily CO_2.

The soil is an essential component of the natural milieu of the World's land. In a broad sense, the soil has arisen as a product of interaction between rocks, water, vegetation, and a number of other factors. Disturbance, however small, of any of these factors entails a change of the soil. For this reason, each natural landscape exhibits its specific soil type.

V.V. Dokuchaev, the founder of genetic soil science and an eminent scientist and thinker, regarded the soil as a "natural historical body". He meant to say that the natural conditions (and, consequently, the soils) are subject to alteration not only in space, but also in time. This idea has been borne out by paleogeographic and paleogeochemical findings.

The spread of the terrestrial living matter has given rise to the formation on the land surface of a specific biogeochemical entity which was absent in the benthic areas of the ocean. The emergence of the soil as a biolatent body was associated with a specific developmental phase of the Earth's living matter.

One of the fundamental attributes of the living matter is the tendency to an ever-increasing renewal of living mass and to a maximal occupation of the available space (a law first formulated by Vernadsky). In the ocean, the massive growth of living matter is severely inhibited. The photosynthetic organisms are localized within the subsurface oceanic layer, and the increase of their mass is limited by the low concentration of nutritional elements in sea water. This limitation is balanced by the high rate of life cycles of the organisms that constitute the living matter of the ocean.

For this reason, most chemical elements, needed by the living matter are not eliminated from the system of closely linked biological cycles of various groups of organisms. The relatively small biomass of photosynthetic micro-organisms assimilates, in the course of biological cycles that multiply repeated each year, essentially the same amount of chemical elements.

The trophic conditions on land are more favourable. The practically unlimited availability of most chemical elements in the Earth's crust creates the possibility

for a progressive mass production of living matter on land, in striking contrast to the oceanic conditions. It is to be inferred therefore that the propagation of the living matter within the World's land space was an inherently predetermined event. Nonetheless, the colonization of the land by living organisms has met with substantial difficulties.

The growth of biotic mass on land is controlled, on the one hand, by the hydrothermal conditions, primarily, atmospheric humidity (since life is impossible in default of water), and, on the other hand, by the availability of accessible forms of chemical elements needed by the organisms that synthesize the primary organic matter. An impediment to global expansion of living organisms on land was first low (if any) concentration of accessible forms of chemical elements in certain rocks. Second, more or less lengthy seasons of insufficient moisture or even total lack of water, inhibitory to living organisms, impair also the regular supply of nutritional elements.

The soil biolatency has arisen as a natural mechanism functioning to counteract unfavorable environmental conditions and providing for the development of photosynthetic organisms. With the passage of geological time, this mechanism became more refined and assisted the spread of living matter on the land surface. The soil, initially localized in separate areas near the coastal strip of seas and internal reservoirs, gradually expanded over the entire land as a thin, virtually continuous coating termed *the pedosphere* by Vernadsky (1936).

The emergence of pedosphere and the colonization of the World's land by living matter have entailed both quantitative and structural alterations in the living matter itself and produced impact on the overall dynamics of global biogeochemical processes.

The biolatent system of the soil has evolved as an optimal natural mechanism for provision of the biotic activity of photosynthetic plants, the producers of the primary organic matter as a basis for the development of biocenoses. In further course, owing to the involvement of various interrelated biogeochemical processes, the soil has become a medium assisting in the interaction of all factors and components constituting a given ecogeosystem (landscape). This interaction is effected via continuous cyclic migration of chemical elements.

The pedosphere, expanded over the entire surface of the World's land, has gained importance as a major link and regulator of the global cyclic processes in the mass exchange of chemical elements. The pedosphere is in equal measure linked, through elemental mass exchange, with the Earth's crust, living matter, and atmosphere. The pedosphere mediates in the mobilization of chemical elements which become involved in aqueous migration to be carried over into the ocean. The pedosphere is a major supplier of air-borne soil particles that form continental aerosols transportable to long distances, in part beyond the land confines. Concurrently, the pedosphere is the recipient of the atmospheric precipitation that deposits chemical elements, including those taken up from

the ocean surface. And, what is the most essential, the grandiose cycle of chemical elements in its entirety originates and terminates in the pedosphere. All of the above-mentioned processes are basically biogeochemical. In the light of our current knowledge, the pedosphere may be regarded as a planetary entity which makes possible the performance of a mechanism controlling the global cyclic processes of elemental mass exchange through a complex system of interdependent equilibria.

4.2. Pedosphere as a Regulator of Carbon-Oxygen Metabolism in the Biosphere

The soil is characterized by a high biogenic capacity and abundance of living organisms and their metabolites as well as by dead organic matter, mostly of vegetable origin. The degradation of plant remains is carried out by the soil mesofauna which is represented by numerous invertebrates, the residents of the upper soil horizons rich in organic matter. The live density of invertebrates in humid soil landscapes varies from 9 to 60-70 ton/km^2 of wet mass, reaching occasionally 200 ton/km^2 (Chernov 1975). Most of the soil invertebrates are accounted for by earthworms (*Lumbricidae*) (to 40-50 ton/km^2) and by *arthropods* (to 10-30 ton/km^2). The available data (Glazovskaya 1981) can give an idea of the activity of earthworms: in an area of 1 km^2 of deciduous forest, they can pass, during one season, about 150 tons of leaf litter and mix the digested products with a mineral mass 10 times as large.

Microorganisms (bacteria, actinomyces, fungi, algae, protozoa) play an important role in the global chemistry of pedosphere. The large number of edaphic species and their diversity show clearly that the soil is a favourable milieu for their habitation. The mass of microorganisms within the upper horizon reaches, per unit area, 2-3 ton/ha, which is several times the respective specific mass for terrestrial animals. The overall live weight of microorganisms in all the pedosphere seems to be close to $10n \cdot 10^9$ tons; the dry weight of edaphic microorganisms is equal to $7 \cdot 10^9$ tons, according to the data by Bowen (1966).

The bacteria constitute one of the major groups of soil microorganisms. Their number varies from $0.5\text{-}0.8 \cdot 10^6$ per hectar (podsol) to $2\text{-}2.5 \cdot 10^6$ (chernozem), which is in a rough correspondence with the range of 2 to 6 tons of live weight per hectar. According to Zavarzin (1984), the bound carbon accounts for $6 \cdot 10^9$ tons of the total mass of soil bacteria, which corresponds to some $12 \cdot 10^9$ tons of dry organic matter.

Bacteria are mainly composed of proteins; lipids are present in lesser amounts. The average contents of major elements in bacteria, according to Bowen (1966), are as follows (in %, on a dry weight basis of organic matter):

C – 54.0	Mg – 0.70
O – 23.0	Ca – 0.51
N – 9.6	Na –0.46
H –7.4	

Enormous masses of chemical elements are involved in the biogeochemical processes associated with the biotic activity of soil bacteria. By way of example, the autotrophic nitrifying bacteria produce during one year hundreds of kilograms (per hectar) of nitrates, assimilable by plants, through biochemical oxidation of ammonia inaccessible to higher plants. The nitrogen-fixing bacteria capable of absorbing and binding the atmospheric molecular nitrogen accumulate $44 \cdot 10^6$ (Delwiche 1970) to $175 \cdot 10^6$ tons of nitrogen (Skinner 1976) per year.

Of particular importance is the activity of heterotrophic bacteria involved in the conversion of organic matter to an end product of biochemical oxidation, carbon dioxide. One cannot omit mentioning the role of actinomyces and fungi which are capable of degrading the most resistant components of plant remains, cellulose and lignin. The actinomyces are present in the soil in quite large numbers frequently reaching billions of species per gram of soil. Thus, the bulk of carbon dioxide produced on land is a result of biotic activity of microorganisms abundant in the pedosphere.

As has been noted above, the soil, owing to its specific micromorphology, possesses a high porosity. The overall volume of voids and pores in the upper soil horizon accounts for 55-70%, or even more, of the total soil volume. Thus, about half of the soil volume is taken by soil air and soil solution. This renders possible the participation of quite significant air masses in the gas exchange between the pedosphere and the lowermost tropospheric layer. However, their assessment can be made only in a very approximate manner. The World's land territory (except the intracontinental reservoirs, $2 \cdot 10^6$ km^2, and the glaciers, $13.9 \cdot 10^6$ km^2) amounts to $134 \cdot 10^6$ km^2. The average porosity of the uppermost layer of the pedosphere 0.5 m deep may be taken equal to 50%. Consequently, the overall volume of soil voids and pores will be $33.5 \cdot 10^6$ km^3. Taking into account that during the warm season of the year the complete renewal of soil air proceeds at a rate of several cycles per day, it becomes apparent that, during one year, many billions of cubic kilometers of gases are involved in the gas transport at the soil-atmosphere interface.

The soil serves not only as a reservoir for natural gases; it also provides, as G.A. Zavarzin remarked, a "perfect facility" for the transformation of gas composition. A very large specific area per unit volume of soil, the abundance of organic remnants, the permanent availability of both the capillary moisture and gas-phase oxygen — all these are factors that stimulate the intensive microbiological activity. The aggregation of the soil matter is of particular importance. The permanent presence of capillary water inside the soil aggre-

gates, and the inter-aggregate pores and fissures free of water provide favourable conditions for the coexistence of various assemblages of microorganisms. In the inter-aggregate space, owing to the free diffusional gas exchange with the surface air layer, the biotic activity of aerobic microorganisms is very intense. Inside the soil aggregates, with their pores filled with capillary water, the situation is quite different, and the diffusion processes in the aeration pores here are incomparably slower. Such conditions are favourable for the prosperous existence of anaerobic bacteria. Finally, the soil provides for a unique system of aerobic and anaerobic microorganisms coexisting in an intimate trophic interaction. The anaerobic microorganisms produce gases from decomposable plant remains. Specific aerobic bacteria capable of oxidizing hydrogen, methane, and various sulfurous compounds prevent the release of these gases from the soil into the atmosphere. Thus, the soil provides conditions for a nearly closed cycle involving the above gases, and practically the only species released into atmosphere is CO_2.

Dr. H.-J. Altemüller (Institute of Soil Management, Braunschweig, Germany) has obtained, using the luminescence effect, excellent microphotographs enabling him to clearly discern that the surface of soil microaggregates is a habitat for communities of microorganisms. Functionally, they absorb oxygen and release CO_2 and some other gases.

Compositionally, the soil air differs appreciably from the atmospheric owing to the intense biotic activity of microorganisms. In the soil air, the concentration of carbon dioxide is higher by two or three orders of magnitude than that of atmospheric air; by contrast, the oxygen concentration is lower. The content of molecular nitrogen is about the same in both. The soil air is rich in water vapor (whose saturation is close to 100%) and in various organic and inorganic biogeneous compounds. The data summarized in Table 4.1, give an idea of the soil air composition.

It should be emphasized that the soil microflora plays quite an important role in the control over soil release of the gases normally present in the atmosphere in very small amounts, including the gases supplied from the inner layers on the Earth's crust. In the telluric gas emanations permanently present are hydrocarbons produced in the metamorphism of sedimentary rocks containing dispersed organic matter. The incessant influx of dispersed hydrocarbons is intercepted by the aerobic bacteria capable of oxidizing these gases. The aerobic bacteria are ubiquitous in soils at a population of $n \cdot 10^3$-$n \cdot 10^5$ species per gram of soil (Zavarzin 1984). Owing to the activity of these bacteria, the terrestrial air is devoid of such hydrocarbons as propane and heptane which actively diffuse towards the crustal surface from oil deposits and gas pools. The increase of hydrocarbons in the soil air brings about an immediate increase in the number of respective bacteria. An increased population of hydrocarbon-oxidizing bacteria can be used as an indicator in gas-and-oil prospecting (the

Table 4.1. Gas Content in Soil Air (after Zavarzin *et al.* 1985)

Gases	Content in soil air (% by volume)	Gases	Content in soil air (% by volume)
N_2	68-73	H_2S	$2 \cdot 10^{-7}$
O_2	5-21	COS	$2\text{-}25000 \cdot 10^{-7}$
CO_2	0.1-20	CH_3SH	$3 \cdot 10^{-7}$
CO	$1\text{-}8 \cdot 10^{-6}$	$(CH_3)_2S$	$1 \cdot 10^{-6}$
H_2	$1\text{-}8 \cdot 10^{-6}$	CH_3SCH_3	$1\text{-}12 \cdot 10^{-7}$
N_2O	$2\text{-}40 \cdot 10^{-5}$		
NO	$1\text{-}10 \cdot 10^{-4}$	Hydrocarbons:	
NO_2	$2\text{-}4 \cdot 10^{-6}$	CH_4	$1\text{-}8 \cdot 10^{-7}$
SO_2	$3 \cdot 10^{-7}$	$C_2\text{-}C_{20}$	$1\text{-}35 \cdot 10^{-6}$

so-called microbiological method of prospecting). Thus, a specific biogeochemical filter is operative in the pedosphere: the bacterial system protecting the atmosphere from the invasion of dispersed hydrocarbons. In connection with the gas-regulating role of the pedosphere, another important biogeochemical, as yet poorly understood process should be mentioned. Many researchers believe that the methylation of metals, primarily, of mercury, is effected by bacteria. Simultaneously, one of the morphologic groups of bacteria, the hyphobacteria, are capable of utilizing various methylated compounds.

Zavarzin (1984) has put forward an idea that a mechanism is operative in the soil enabling it to entrain the methylated species into the intraedaphic cycle and to protect thereby the atmosphere from the influx of methylated compounds. It seems logical therefore to presume that, in view of the above mechanism, a lesser release of volatile methylated metals is expected from the land surface than from the ocean surface.

The gas exchange between the soil and the lowermost tropospheric layer is effected owing to diffusion and convection. An excessive humidity, the more so the saturation of the soil with water, inhibit the production of carbon dioxide by microorganisms. Simultaneously, the anaerobic microbiological processes become intensified leading to the formation of methane, hydrogen sulfide, and methylated mercury.

In automorphic, well-aerated soils, with the predominance of the aerobic microflora over the anaerobic, the soil air oxygen concentration tends to slightly decrease down the soil profile, whereas the CO_2 content is seen to increase two-fold. In hydromorphic soils, the water-filled pores impede aeration, which stimulates anaerobic microbiological processes. Under the conditions of incomplete water saturation, the soil air oxygen content declines markedly down

the soil profile, with the concomitant several-fold increase in CO_2 level. The distribution of O_2 and CO_2 in automorphic and hydromorphic soils at the period of highest biological activity (June) is shown in Table 4.2. The increase in CO_2/O_2 ratio is attended by intensification of the anaerobic microbiological processes producing methane, hydrogen sulfide, ammonia, methylated metal species, in particular, methyl- and dimethyl-mercury.

The solid matter of the soil is the more active adsorbent for water vapor than for other gases; commonly, the content of water vapor in the soil is predominant, which results in a smaller uptake of other gases by the solid phase of the soil. By their uptake by the soil, the air components follow the order:

$$H_2O > CO_2 > O_2 > N_2$$

Some telluric gases diffusing towards the surface from the site of their occlusion across the bedrock are occasionally found as soil air components. For example, the soil overlying accumulations of radioactive elements may become enriched in radiogenous emanations (radon), and the soil over sulfide ores, in mercury vapors. The phenomenon of elevated concentration of extraneous gases in the soil constitutes a basis of atmogeochemical methods of prospecting for minerals.

Thus, the pedosphere is a domain into which are merged two branches of the grandiose carbon-oxygen mass exchange cycle whose performance is a major condition for the existence of the biosphere. On the one hand, the soil provides for the production of terrestrial photosynthetic plants that bind carbon dioxide to form organic matter and to release free oxygen as a metabolite. On the other hand, the soil serves as a medium for degradation of the dead organic matter, its biochemical oxidation to carbon dioxide and the release of the latter into atmosphere. Considering these processes, the soil plays the role of a central link in the global carbon-oxygen cycle and, like the ocean, performs regulatory functions in the geochemical regime of the atmosphere.

The quantitative estimates of carbon dioxide production by separate types of soil and by pedosphere as a whole strongly differ among themselves according to various authors. As reported by Zavarzin *et al.* (1985), the gley peat soils of tundra release about 0.3 ton/ha $year^{-1}$ of CO_2; the podsolic soil of coniferous forests, 3.5 to 30; the brown and gray soils of deciduous forests, 20 to 60; the chernozem soils of steppes, 40 to 70.

One may try to estimate the CO_2 mass exchange in the pedosphere-vegetation system of the World's land in terms of the annual production balance of photosynthetic plants. The use of such an approach is based on the following considerations.

The terrestrial vegetation mass within a period of 10-12 thousand years after the last glaciation to the onset of human productive activities persisted in a

Table 4.2. Distribution of O_2 and CO_2 down the Profile of Automorphic and Hydromorphic Soils of Different Natural Zones (after Zavarzin *et al.* 1985)

Automorphic soils				Hydromorphic soils			
Sward-podsolic		Southern chernozem		Peat-boggy		Meadow-alluvial chernozem	
depth, cm	CO_2/O_2 (% by volume)	depth, cm	CO_2/O_2 (% by volume)	depth, cm	CO_2/O_2 (% by volume)	depth, cm	CO_2/O_2 (% by volume)
7	0.9 / 20.0	10	0.70 / 20.55	10	0.98 / 19.40	25	2.5 / 18.5
15	1.2 / 19.8	20	0.80 / 19.60	20	4.96 / 16.55	50	3.2 / 17.8
25	1.6 / 19.3	30	0.85 / 19.80	30	5.45 / 15.55	75	6.3 / 13.7
45	2.3 / 18.4	40	1.15 / 19.80	60	6.92 / 14.30	100	6.6 / 13.6
110	1.8 / 19.0	50	1.30 / 19.50			150	6.8 / 13.4
210	1.5 / 19.4	100	1.45 / 18.85			200	5.2 / 15.6

state of dynamic equilibrium. Certainly, in accordance with the secular variations of humidity, there occurred slight fluctuations of the total biomass, however, without clearly defined trends to continuous growth or degradation. This signified that the annual amount of CO_2 absorbed by photosynthetic plants was close to the amount of CO_2 annually released by the soil cover of the World's land.

The amount of carbon that the terrestrial vegetation could bind by photosynthesis was equal, prior to the intervention of man, to $86 \cdot 10^9$ ton/year. Presumably, roughtly the same (or, perhaps, somewhat lesser) amount of carbon in the form of carbon dioxide could be released by the pedosphere. As noted above, owing to the productive activity of man, the vegetation has reduced by about 25%. Therefore, the mass of carbon dioxide as supplied by pedosphere amounts to some $230\,10^9$ tons. This value is close to that estimated by Dobrodeyev *et al.* (1976), but is much in excess of the data by Houghton *et al.* (1986).

In reality, the migration cycle of carbon mass exchange in the system "atmosphere-land vegetation-pedosphere-atmosphere" should not be regarded as a completely closed one because of the loss of certain amount of carbon from the migration cycle and the preservation of this element as a component of dead organic matter. This makes up only a small percentage to the total of carbon involved in the annual biogeochemical cycle. The organic matter which is annually eliminated from the carbon-oxygen cycle contains the amount of bound carbon making up about 1% of the mass of CO_2 annually uptaken by the plants (Dobrodeyev *et al.* 1976).

Despite the small percentage of the carbon mass lost from the global biogeochemical cycle, the openness of this cycle has far-reaching consequences. The availability of plant remains (forest litter, peat) and soil humus provides for the occurrence of oxygen in the atmosphere. Oxygen has been preserved only because it escaped its being consumed by microorganisms in the biochemical oxidation of dead organic matter.

4.3. Organic Matter of the Pedosphere

The organic matter is one of the most important components of the pedosphere. In the foregoing subsection, the effect of an open global carbon-oxygen biogeochemical cycle has been discussed as well as the importance of a permanent reserve of organic matter for the composition of the atmosphere and the occurrence in it of free oxygen. The organic matter produces a powerful effect on a variety of processes occurring in the pedosphere.

A tremendous mass of organic matter, mostly of vegetable origin, is annually supplied to the pedosphere. Depending on the bioclimatic conditions, the supply of dead organic matter in various areas of the World's land (excepting glaciated territories and absolute deserts) varies within a range of 1.0 to 25.0 ton/km^2 per year. The annual overall mass of dead organic matter (including the damage caused to natural vegetation by man) amounts to $125–130 \cdot 10^6$ tons.

Different amounts of compositionally dissimilar plant remains, distinct specificity and intensity of microbiological activities, diversity of hydrothermal conditions—all these factors contribute to the buildup of a complex system of organic compounds found in the humus. Compositionally, the humus is variable, it is permanently renewed owing to the synthesis and degradation of its constituents.

Three major groups are distinguished in the organic matter of the soil.

The first group is represented by decayed, at advanced or incipient stage, remnants of mostly vegetable origin. They form the forest litter and peat felt. This is the so-called coarse humus. When viewed under a microscope, it reveals all details of the vegetable tissue, such as cell configuration, cell membranes, and so forth. Less resistant tissues (cambium, phloem, primary bark parenchyma) are in a degraded state.

The second group includes remnants at a stage of profound transformation which form a black friable matter. The examination using a microscope will show that this matter is composed of finely divided and deeply transformed plant remains: detrital fragments of vegetable tissues and relict cell elements, all mixed with a profuse variety of newly formed organic compounds. This form of the organic soil material is referred to as *the moder.*

The third group consists of specific organic soil formations, with no visible structural signs of vegetable tissues, which constitute the humus proper. These are amorphous aggregates seen as transparent pale-yellow or opaque dark-brown under the microscope. In some soils, the humic matter is diffusely dispersed in the soil matrix, in others, it is glued to small-sized mineral particles forming a type of humus known as *the mull.*

The above-mentioned forms of organic soil matter require a good aeration for their buildup. In soils exposed to a lengthy period of water saturation, the activity of mesofauna and aerobic microorganisms is inhibited. A consequence of this is the highly retarded transformation of the plant remains. Under such conditions, peat is formed from the remains of hydrophilic plants, mainly mosses. Its characteristic features are a low degree of decomposition of plant remains (less than 30%) and the fibrous structure owing to the predominance of mosses among the peat-forming species. The organic soil matter composed of peat components constitutes a type of humus known as *the moor.*

All of the above forms of organic soil matter grade indistinctly from one into another.

The available evidence allows one to infer that the organic soil matter is made up of slightly transformed plant remains, products of their disintegration and of initial digestion by mesofauna and certain microorganisms, as well as of specific organic soil matter. The two last-mentioned categories constitute what is properly known as the humus.

The transformation of organic matter in soil is effected owing to the activity of microorganisms. Various microorganisms and their specific enzymes interact with definite components of plant remains. The nonspore-forming bacteria utilize the most accessible components: simple hydrocarbons, amino acids, simple proteins. The cellulose-fermenting bacteria decompose resistant carbohydrates. The actinomyces bring the process to an end through digesting the most resistant components of plant remains and humic matter.

The formation of humic matter involves two types of processes. The processes of the first type result in a partial decomposition of organic compounds to simpler ones. For example, proteins become split to form amino acids, carbohydrates to simple sugars, and so forth.

The processes of the second type are much more complex. A major reason for this is that the hydrolysis of organic polymers terminates, if the enzyme meets with an irregularity in the polymer structure. By way of example, one may refer to a case when the enzyme, specialized in hydrolysis of cellulose, runs across a lignified part of a polymer. The remnants of resistant species accumulate to be used as a starting material for specific condensation reactions. These reactions, not encountered in biological polymerization processes, lead to quite stable products.

The second type processes effect the coupling of aromatic phenolic compounds (products of lignin and cellulose degradation) to amino acids (products of decayed microorganisms). In the course of oxidation and condensation, carboxylic groups are formed which, along with phenolic hydroxyl groups, impart an acidic character to the humic matter. The major components of humus are humic and fulvic acids, their salts, as well as humin which is a specific material made up of humic acids bound to finely-dispersed mineral particles. These components exhibit a variety of gradations.

Humic acids are high-molecular compounds of complex structure. According to Orlov (1974), the structural cell of humic acids from sward-podzolic soil has a stoichiometric formula of $C_{173}H_{183}O_{86}N_{11}$; that from chernozem, $C_{73}H_{61}O_{32}N_4$; the structural cell of fulvic acids from sward-podzolic soil is $C_{270}H_{318}O_{206}N_{16}$, and from chernozem, $C_{260}H_{280}O_{177}N_{15}$. The compositional content of carbon in humic acids varies from 40 to 60%, of nitrogen, from 3.5 to 6%. Fulvic acids contain less carbon and nitrogen, respectively, from 35 to 50% and from 3 to 4.5%.

The major structural units of a complex molecule of humic acid are a fused central part (core), side chains, and peripheral functional groups: carboxylic,

Table 4.3. Heavy Metal Concentration in Humic Acids from the Podzolic Soils of the North-Western European Part of the USSR (after Saprykin *et al.* 1984)

Soil	Heavy metals, mg/kg of dry weight							
	Cu	Zn	Pb	Ni	Co	Mn	V	Mo
Weakly sward-podzolic gleyic soil								
humic acids	6.0	10.0	0.2	1.6	0.4	10.0	40.0	0.4
fulvic acids	25.0	100.0	0.4	15.0	0.9	5.0	4.0	—
Medium sward-podzolic soil								
humic acids	8.0	16.0	0.6	0.6	0.2	2.0	6.0	10.0
fulvic acids	15.0	150.0	3.0	5.0	1.4	1.5	0.5	—
Podzolic illuvial-ferruginous soil								
humic acids	6.0	5.0	0.2	—	—	2.0	0.2	2.0
fulvic acids	15.0	20.0	15.0	5.0	0.5	0.5	—	1.0

COOH; phenolic hydroxyl, OH; methoxy group, OCH_3; carbonyl, C=O; quinone carbonyl, C=O. The core is made up of fused aromatic and heterocyclic rings, and the side chains, of carbohydrate, amino acid and other groups. The reactivity of humic acids should be attributed to the carboxyl and phenol-hydroxyl groups, with their hydrogen replaceable by other cations. In the soil, of most frequent occurrence are not free humic acids, but their salts, humates of calcium, magnesium, and other metals. Some hydrogens in the functional groups may be replaced by complex cations of type $Fe(OH)_2^+$ and others. Finally, structurally complicated intracomplex compounds (chelates of iron, aluminum, and other metals) are formed. Humic acids are insoluble in water, but are readily soluble in alkali solution.

Fulvic acids are structural congeners of humic acids, with the dominance of side chains over the core. The percentage of carboxyl and phenol hydroxyl groups is larger over that of humic acids. Fulvic acids are soluble in water, the aqueous solutions exhibiting a strong acid reaction (pH 2.6-2.8). The dissolving power of fulvic acids is further enhanced by their propensity to chelation. Complexed fulvates are capable of actively migrating in natural waters under the conditions when free metal cations deposit a precipitate.

Since fulvic acids contain more functional groups than humic acids, the heavy metals prefer binding to the former. A study of the metal distribution in humic acids isolated from podsol soils of the north-western European part of the USSR has shown copper, zinc, lead, and cobalt to occur in fulvic acids in higher concentrations. However, the concentration of manganese, vanadium, and molybdenum is higher in humic acids (see Table 4.3).

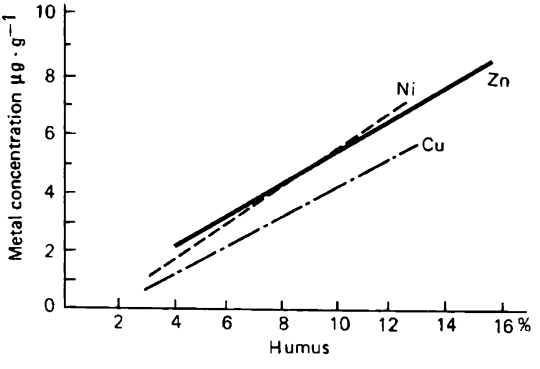


Fig. 10. Relationship between the soil concentration of heavy metals and the humus percentage

Rabinovich (1969) analyzed heavy metal concentrations in humic acids extracted from widespread soils of Moldavia. As has been found, the metal concentration in humic acids was appreciably higher not only over that in the soils of interest, but also higher over the average metal concentration in the World's land vegetation. For example, in the chernozem humic acids (which are the most essential humic components of this type of soil), the concentration of zinc is more than twice the average concentration of this element in the land vegetation, of vanadium, 17 times as large, of chromium and cobalt, even higher.

The selective binding of trace metals with the water-soluble components of humus (fulvic acids), or with the immobile gels of humic acids is an essential factor in the involvement of metals in migration cycles or, conversely, in their removal from the migration and their fixation in the soil (Fig. 10).

Thus, the humus plays a dual role. On the one hand, it acts as a source of nitrogen and other elements which are primarily essential for higher plants and which are released from the organic matter owing to microbiological activity. Therefore, the humus is an important factor in the productivity of phytocenoses and the soil fertility. On the other hand, humic acids and their derivatives, owing to the specificity of their molecular structure, exert an active influence on the migration and accumulation of chemical elements in the pedosphere. For this reason, the humic matter is an important factor in the regulatory mechanism of migratory fluxes in the pedosphere.

The dead parts of plants are annually supplied to the soil as sheddings (leaf fall). The amount of the shed material is not proportional to the mass of vegetation. For example, the silvan communities of the southern taiga with their enormous biomass (over 300 ton/ha of dry matter) supply annually to the soil some 5 ton/ha of dry organic matter, whereas in the meadow steppe vegetation with an appreciably smaller biomass (25 ton/ha), the supply of shed material is three times as large.

A significant part of plant remains are confined to the soil surface as forest litter in forests, as grass felt in herbal communities, as peat accumulations in waterlogged landscapes. The permanent presence of plant remains indicates that their degradation proceeds at a slower rate than the supply of dead parts from plants.

The digestion of plant remains by the mesofauna and microorganisms into humus may be estimated quantitatively by the ratio of the amount of dead organic matter on the soil surface to its amount as supplied annually through shedding. According to the data by Rodin and Bazilevich (1965), the highest ratio, 90, has been recorded for tundra landscapes. This fact signifies that, under the severe conditions of tundra, the biotic activity of edaphic mesofauna and microorganisms is strongly inhibited, and it takes 90 years for the total of one-year litter production to be completely digested; accordingly, the biological

cycle of chemical elements is also strongly retarded. In steppe landscapes, the reported ratio is 1.0–1.5, implying that the total amount of shed material is digested within one year. In a desert, this process is still more rapid, since the plant remains on the soil surface are practically absent. In silvan communities, the ratio in question is dependent on the hydrothermal condition and the duration of the warm season permitting the biotic activity of mesofauna and microorganisms. In the soil of taiga forests, the complete digestion of plant remains takes 20–30 years, in the broad-leaved forests of temperate climate, it is 3–4 years, whereas in the equatorial rain forests, several digestion cycles are operative within a period of one year.

Rapid decay of plant remains occurs under the conditions of a free gas exchange between the soil and the atmosphere, which stimulates the aerobic meso- and microbiological activity. In waterlogged areas, where the dead organic matter is saturated with water, the gas exchange is impeded. Under such conditions, the activity of aerobic organisms is inhibited, the decay of plant remains is retarded, which leads to peat formation. This process is favored by the occurrence in the peatland waters of soluble organic compounds with aseptic properties. As a result, half-decayed plant remains can persist in peatland deposits for thousands of years.

The biogeochemical transformation of organic matter in the soil is not confined solely to the digestion of plant remains into humus. By the action of microbiological activity, the process continues to a complete degradation of organic matter yielding CO_2 as the end metabolite. One may estimate the period of humus renewal from the measurement of the absolute age of humic acids and humates by radiometric dating method using the carbon-14 isotope with its half-life of 5678 years. The results obtained have provided evidence that the humus renewal in the upper horizon of modern soils takes a period of 300–500 years. In the deeper horizons, the renewal proceeds at a far-slower rate, and thus the humic matter has the age of several thousand years. Presumably, this should be attributed to a higher population of living organisms in the upper soil horizon. The amount of humus decreases down the soil profile parallel with the decreasing population of microorganisms (Fig. 11).

The overall mass of dead organic matter of the pedosphere is composed of three major ingredients: (i) half-decayed plant remains of forest litter, (ii) peat accumulations, and (iii) thoroughly transformed organic matter of the soil (humus). The forest litter mass of the pedosphere not impaired by the productive activity of man has been estimated by Rodin and Bazilevich (1965) to amount to $193.8 \cdot 10^9$ tons of dry matter. With allowance made for the deforestation because of the land development for agricultural needs, the above estimate should be lessened by 5%.

The humus, as a rule, is confined to the upper soil horizon; it should be noted that the depth of this horizon, the quantity and composition of humus

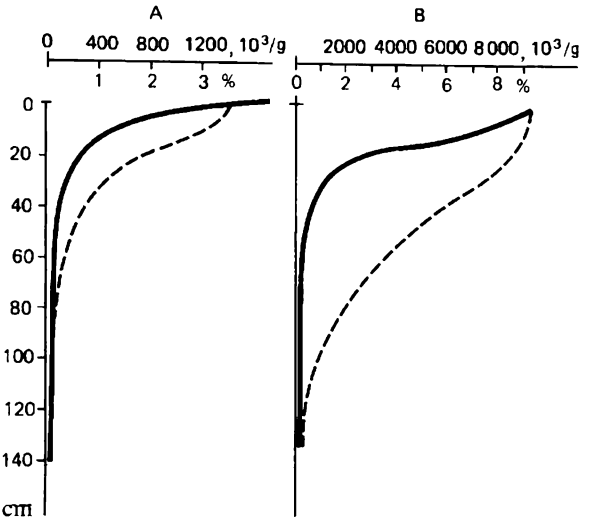


Fig. 11. Distribution curves for microorganisms (solid line) and organic matter (dashed line) down the soil profile
A—podsolic soil; *B*—chernozem soil

differ strongly in different soils. One may estimate quantitatively the water-soluble fulvic acids as produced by the decay of forest litter of different types of soils by analyzing the lysimetric water for the loss of elements (D'yakonova 1972). One square meter of the spruce forest litter overlying the podsol soil produces annually 2600 to 4140 mg of soluble organic matter and 50 to 84 mg of iron oxide bound with the soluble organic matter. The oak forest litter on chernozem supplies less soluble organic matter less by two orders of magnitude, 50 to 80 $mg/m^2 \cdot year^{-1}$, and a mere 3 to 10 $mg/m^2 \cdot year^{-1}$ of bound iron. Apparently, the podsol soil microorganisms produce mostly fulvic acids in digesting the litter, whereas the chernozem microorganisms produce preferably water-insoluble gels of humic acids and calcium humates. The humus content in forest soils varies, depending on the climatic conditions, from 2 to 6%. The high humus content is associated with herbaceous vegetation. The highest humus percentage has been recorded for the chernozems underlying meadow mixed-fodder grasses, 6 to 12%, occasionally reaching 20%. The overall humus reserves in the pedosphere have roughly been estimated as $2.5 \cdot 10^{12}$ tons (Kononova 1974). However, the earlier estimations (Eglinton and Murphy 1969) gave a value for the humus mass available in the pedosphere less by an order of magnitude — about $0.1 \cdot 10^{12}$ tons.

The mass of incompletely decayed peat material is quite significant. The conditions of a cold and humid climate are favorable to the accumulation of peat reserves. The overall peat reserves within the World's land confines amount to $495 \cdot 10^9$ tons of dry matter, the greater part of those ($289 \cdot 10^9$ tons) being found in the boreal belt of Eurasia.

The above data, pieced together, allow one to conclude that the total mass of dead organic matter, contained in the pedosphere comes to about $3.2 \cdot 10^{12}$ tons. This is nearly 1.5 times as large as the mass of the extant land vegetation and is by a factor of 25 in excess of its annual production.

Along with the decay of dead plant organs to organic matter, the accumulated chemical elements therein undergo redistribution. The compositional comparison of the green, vegetative and deciduous tree organs (needles and leaves) and the forest litter will reveal an increase in the relative content of some elements and a decrease of others. The data summarized in Table 4.4 allow one to presume that the chemical elements contained in the least resistant vegetable tissues are removed from the litter matter. Such elements are potassium, magnesium, sodium, phosphorus, sulfur, and partly calcium. The content of other elements, presumably consisting of more resistant tissues, tends to increase. In particular, this behaviour is typical of metals and silicon. The abundance of silicon in some plants is so large that it forms the phytolyths which are microscopic bodies of amorphous silicon oxide (plant opal), also stored in the litter. Alongside of this, a variety of trace elements are prone to be actively taken up by the litter owing to the enormous specific surface of half-decayed plant sheddings.

The most complete evidence on the contents of heavy metals and other trace elements is available for the organic matter of peat. Peat forms under the conditions of excessive soil humidity, impeded gas exchange and, consequently, suppressed microbiological degradation of plant remains. The peat formation is favored by a cold humid climate. Large peat accumulations are found in the boreal belt of the northern hemisphere extending to an area of $1.5 \cdot 10^6$ square kilometers.

Peat is made up of incompletely decayed (by 20–30%) remains of marsh plants. Peat contains, as compared to the terrestrial vegetation, more resistant components in its organic matter (lignin, bitumen). The average peat composition is: carbon, 56%; hydrogen, 6%; oxygen, 35%; nitrogen, 1 to 3.5%; and sulfur, 1.5% (Glazovskaya 1988).

Two types of biogeochemical environmental conditions are distinguished for peat accumulation. The first type is characterized by excessive soil humidity due to precipitation, slow soil water evaporation, and impeded drainage in watersheds of plains. Such conditions are favorable for the formation of the so-called raised bogs (or raised mosses) where major peat-forming plants are sphagnous mosses *Sphagnum fuscum*, *Sph. magellanicum*, and others. The raised-

Table 4.4. Concentration of Chemical Elements in the Deciduous Plant Organs and Forest Litter in the Phytocenoses of the USSR (compiled by the author after the data of Rodin and Bazilevich 1965)

Plant, territory	Object analyzed	Elements (%, by dry weight)										
		K	Mg	Na	P	S	Ca	Mn	Si	Al	Fe	Total
Eriophorum vaginatum, tundra, Yakut region	(a)	0.32	0.14	0.07	0.15	—	0.19	0.02	0.25	0.12	0.03	1.29
	(b)	0.10	0.14	0.10	0.12	—	0.26	0.06	0.35	0.19	0.11	1.39
	(c)	0.12	0.16	0.10	0.20	—	0.91	0.20	0.85	0.49	0.26	3.29
Pinus silvestris, taiga, the Kola Peninsula	(a)	0.27	0.08	0.02	0.04	0.03	0.34	0.08	0.04	0.05	0.01	0.96
	(b)	0.11	0.09	0.02	0.04	0.04	0.54	0.09	0.07	0.03	0.03	1.06
	(c)	0.27	0.16	0.04	0.05	0.06	1.10	0.09	0.88	0.82	0.62	4.09
Picea excelsa, taiga, the Kola Peninsula	(a)	0.52	0.38	0.03	0.07	0.07	0.52	0.07	0.31	0.13	0.01	0.84
	(b)	0.93	0.02	0.02	0.05	0.08	0.93	0.08	0.67	0.09	0.01	0.60
	(c)	0.44	0.14	0.03	0.04	0.08	0.41	0.08	0.44	0.27	0.14	1.15
Quercus robur, deciduous forest of the Srednerusskaya Vozvyshennost'	(a)	1.07	0.12	—	0.10	—	1.16	0.03	0.43	0.03	0.02	3.16
	(b)	0.45	0.22	—	0.17	—	1.64	—	0.45	0.03	0.04	3.00
	(c)	0.14	0.14	—	0.13	—	1.41	—	0.57	0.37	0.18	2.94
Parrotia persica, subtropical forest, Lenkoran'	(a)	0.70	0.23	0.07	0.12	0.01	0.96	0.01	0.97	0.04	0.01	2.15
	(b)	0.20	0.21	traces	0.11	0.03	1.23	0.01	1.09	0.07	0.04	3.04

Objects analyzed: (a) leaves or needles; (b) annual sheddings; (c) forest litter

bog waters as supplied by precipitation exhibit a low mineralization (30-70 mg/l). The mineral content in sphagnous mosses is low, the peat ash content is about 3%. The waters are rich in acid metabolites of sphagnous mosses and water-soluble humic acids, at pH 3.5–4.5. Under such conditions, peat is accumulated at a rate of about 1 mm/year.

The development of sphagnous vegetation is maintained owing to the elements released from half-decayed dead plants and supplied in the rainfall. The ecosystems of raised bogs exhibit a high degree of geochemical autonomy. The occurring biogeochemical mass-exchange cycles therein are poorly communicative with the surrounding landscapes and are open only to the atmospheric migratory fluxes of chemical elements. For this reason, the raised-bog peat ash content is lower than the ash content of the World's land vegetation and is 2.8% (Dobrodeyev 1990).

The geochemical pattern of raised bogs is quite specific. The concentration of water-soluble organic matter in the waters of raised-bog peatlands varies from 20 to 50 mg/l; fulvic acids account for 45–55% and humic acids, for 10–20% of dissolved organic matter. The abundance of water-soluble humic species facilitates the formation of complex and intracomplex metal compounds capable of active aqueous migration. Simultaneously, the migration is hindered by the poor drainage. It should be noted that peat exhibits quite a high sorptive capacity with respect to metals and other trace elements. The measured heavy metal concentrations in the raised-bog peat of Russia are summarized in Table 4.5.

The second type of conditions for peat accumulation is characteristic of lowland bogs confined to negative forms of relief. Here the aqueous saturation of the soil is provided at the expense of high-level ground waters with a neutral or even weakly alkaline reaction (pH = 6-8) and with a degree of mineralization higher than that of raised-bog waters. The mineralization of lowland bog waters amounts to 200 mg/l, or even higher. This is due to the loss of chemical elements from the catchment area soils. In the lowland bog sediments accumulations of Ca^{2+}, Fe^{2+}, Mn^{2+} carbonates, Fe^{2+} and Fe^{3+} phosphates, Fe^{3+} and Mn^{4+} hydroxides frequently occur. The peat-forming plants are represented by hypnaceous mosses, sedge, reed, fern, and bushes. These plants contain mineral substances in appreciable amounts, which cause the ash content of lowland peat to rise to 10%, occasionally reaching 20%.

The conditions for the formation of high and low peatlands are clearly demonstrative of the biogeochemical differentiation of pedosphere which is determined by the geochemical status, that is, autonomist or subordinative, of a given local area. The raised bog exemplifies a geochemically autonomous ecosystem which is independent of the biogeochemical processes in the neighbouring areas. The lowland bog is a geochemically subordinate landscape. Compositionally, the peat of lowland bogs is formed under the influence of

Table 4.5. Average Concentration of Heavy Metals in the Raised-Bog Peat (after Dobrodeyev 1990)

Heavy metal	Concentration (μg/g)	
	in ash	in dry matter
Fe	29000 (16969–204000)	547 (9–7762)
Zn	940 (36–75497)	26 (0.7–50)
Mn	700 (20–6800)	18 (0.2–128)
Ni	180 (16–721)	4 (0.34-11.6)
Cr	120 (32–500)	4 (1.2–12.5)
Pb	120 (0.1–2500)	3 (0.1–43)
Cu	89 (8–335)	2.2 (0.01–23)
Co	45 (25.9–259)	2 (1.2–6.3)
Cd	15.5 (0.85–120)	0.65 (0.03–5)

Note: Variability of results is given in parentheses.

Table 4.6. Average Concentration of Trace Elements in the Peat of Forest Zone in the European Part of the USSR (after V.N. Kreshtapova, personal communication)

Element	Type of peat					
	raised-bog peat (603 samples anal.)		transitional (324 samples anal.)		lowland peat (2657 samples anal.)	
	m, mg/kg	*V*, %	*m*, mg/kg	*V*, %	*m*, mg/kg	*V*, %
Ti	117.9	52	210.6	89	283.8	72
V	3.0	37	6.8	48	10.8	90
Cr	3.7	51	4.9	51	7.8	36
Mn	22.1	99	43.3	98	124.8	93
Co	0.7	81	0.9	73	1.3	90
Ni	4.0	63	4.6	77	7.0	44
Cu	3.6	85	4.7	95	7.5	61
Zn	18.4	97	8.5	90	11.1	72
Ga	1.2	57	2.7	89	3.1	78
Ge	0.4	76	0.2	95	0.6	81
Zr	4.2	83	11.5	97	17.9	64
Mo	0.3	77	1.1	65	1.6	68
Pb	3.6	64	4.5	98	2.3	71
Ag	0.1	86	0.2	105	0.2	73
Y	0.7	68	2.4	48	2.2	95
Sc	0.1	112	0.3	102	0.3	84
Sr	19.6	53	47.5	52	55.4	40

Note: *m* is the average concentration, *V* is the coefficient of variation

biogeochemical processes occurring in the surrounding territories from where certain chemical elements are lost into the lowland bogs to be taken up and accumulated by the local moor vegetation. For this reason, the concentration of heavy metals and other trace elements in the peat-forming plants of lowland bogs is higher than that in the plants of raised bogs.

The average concentrations of trace elements in different samples of peat occurring in the northern European part of the USSR are summarized in Table 4.6. A comparison of the results reveals that the concentration of almost all trace elements is higher in the peat of lowland bogs. An exception to the rule is zinc whose concentration is higher in the raised-bog peat. This fact is quite typical and seems to indicate that zinc is less tightly held in peat than other metals.

4.4. Mineral Matter of Soil and Its Biogeochemical Transformation

The interaction of living organisms with Earth's crust is effected most intensively in the pedosphere. In soils of different type, the mineral matter accounts for 90 to 99% of soil mass. Therefore, the average elemental composition of a soil layer 0.5-1.0 m deep is in fact the composition of the soil mineral matter (except for carbon and nitrogen). The mineral matter of soil is quite heterogeneous, with its components playing different roles in the geochemistry and biogeochemistry of the pedosphere.

The extant soils have mostly formed on loose continental deposits of the Pleistocene and Pliocene-Pleistocene epochs. Various genetic types of those deposits form, in their entirety, a loose unconsolidated mass which overlays the World's land and which has emerged as a result of hypergene transformation (weathering) of rocks during the latest period of the geological history. The depth of the soil cover varies from 10-20 cm on steep slopes through tens of meters on plains and to hundreds of meters or even more in tectonic depressions. The soil cover, depending on its depth, is either in full, or in its upper part incorporated in the pedosphere and is thus a central playground for the interaction of mineral matter with land bios, edaphic meso- and microorganisms, dead organic matter, natural waters, and atmosphere.

The loose covering deposits consist of mixed intermingled and redeposited products of weathering. This is revealed through comparing the average mineral composition of the continental Earth's crust and the loose terrestrial cover. In the Earth's crust, quartz accounts for 12%, feldspar for 51%, ferro-magnesian silicates (olivins, pyroxenes, amphiboles, micas) for 24% (Ronov and Yaroshevsky 1976). In the loose cover, the mineral proportion is different: the content of ferro-magnesian silicates is about 1-2%, and of feldspar, about 10-15%, whereas that of quartz, the most durable rock-forming mineral, increases to 50%, or even more. The change in mineral proportion is due to the fact that most hypogene silicates, subject to hypergenesis during the last million of years, suffered degradation and became partially transformed to hypergene silicates, the clay minerals. Their content in the loose cover is close to 20%. The soils, as they form on loose covering deposits, inherit the mineral composition of the hypergene silicates. Thus, the soil's mineral part is composed of a material transformed by hypergene processes (weathering) long before the buildup of extant soils. Simultaneously, some minerals continue to form in the course of the current pedogenesis.

Heterogeneous components of the mineral part of soils may be classified into three groups:

1. clastic fragments of minerals and rocks;
2. finely-dispersed clay minerals; and

3. recent mineral that arose during the soil profile formation.

Each of the above groups plays a role in soil formation.

1. The clastic minerals exert a strong influence of the overall chemical composition of the soil. The more clastic quartz is in the mineral matter of the soil, the greater is the relative content of SiO_2 and the less of other elements. The greater the amount of clastic silicates, the more aluminum. Accessory minerals, resistant to weathering and therefore present in the covering deposits (ilmenite, magnetite, zircon, rutile, and others) serve as concentrators for numerous trace elements.

The data listed in Table 4.7 show that magnetite is a concentrator for copper; and epidote and sphene for strontium, whereas in zircon, except for the major zirconium cation, scandium is also present in high percentage. Specifically, titaniferous minerals (ilmenite, rutile, sphene) are to be noted as containing more niobium, tantalum, molybdenum, and tin by 2-4 orders of magnitude as compared to the crustal abundance of these metals. However, the accessory minerals are durable and resist the easy release of the elements contained therein that could be involved in biogeochemical processes.

Of greater importance are the trace elements contained in widespread clastic minerals as isomorphous inclusions and confined to the surface of crystal defects (see Section 1.4). In hypergene degradation, the ferro-magnesian silicates release vanadium, chromium, zinc, copper, nickel, cobalt, and the feldspar releases strontium, barium, lead, and rubidium.

Nalovic (1977) has shown in his experiments that in the degradation of clastic minerals, the major and minor chemical elements constitutive of a given mineral are mobilized in a different manner. Some trace elements are mobilized very easily, much before the breakdown of the crystal chemical structure of a mineral. In particular, in extraction of augite, the first portion contained most of the extracted heavy metals, whereas iron, constitutive of the crystalline structure of the mineral, was extracted gradually as the structure suffered degradation (Fig. 12). Apparently, in hypergene degradation or transformation of clastic minerals, the extrastructural forms of trace elements confined to crystal defects are the first to be mobilized; subsequently, other forms become mobilized including the isomorphous admixtures constitutive of the crystal mineral structure.

Thus, the clastic minerals as the most inert components of mineral matter of the soil, contain a limited reserve of comparatively easily mobilizable trace elements. It is noteworthy that the concentration of trace elements in clastic minerals (specifically, in quartz) from the soil or loose covering deposits, is, as a rule, lower than that in the same minerals found in undecayed rocks. This should be attributed to the fact that the mineral fragments as subjected to weathering and multiple redeposition have suffered a severe disintegration, and the relatively loosely held elements became in part leached out.

Table 4.7. Average Content of Trace Elements in Stable Accessory Minerals

Mineral	Element and its content, μg/g										
	Pb	Zn	Cu	W	Sn	Mo	Ta	Nb	Ga	Ge	Sc
Ilmenite	3	867	36	63	99	8	262	2081	4	1	57
Magnetite	24	238	78	5	25	13	62	252	21	3	7
Epidote	32	8	35	6	30	2	nil	18	11	2	13
Garnet	180	10	22	nil	24	7	8	73	25	10	80
Zircon	112	nil	31	66	54	10	40	239	0.4	2.4	143
Rutile	nil	40	27	672	605	183	1500	1872	nil	300	47
Sphene	221	500	30	35	225	82	240	1924	4	2	10
Tourmaline	137	175	12	nil	29	9	30	90	36	35	35

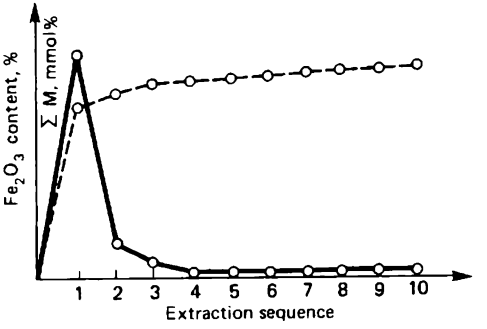


Fig. 12. Extraction of the total of trace metals (solid line) and iron (dashed line) from augite with weak alkali-acid solvents (Nalvoic 1977)

2. The finely-dispersed mineral matter of the soil is mostly composed of hypergene silicates: kaolinite, metahalloysite, montmorillonite, hydromicas, and others. In lesser amounts present are minerals of the iron oxide and hydroxide group, also aluminum as well as X-ray-amorphous compounds.

Dispersion of the mineral matter is a major manifestation of its hypergene alteration on the land surface. Minerals exposed to diurnal and seasonal temperature variations develop microscopic cracks confined to crystal defects, whereas in rocks, such cracks are confined to grain contacts. The disjoining action by water film in fine cracks and by ice stress in larger cracks facilitates the mechanical disintegration of rocks. Concurrently, the hypogene silicates become transformed to hypergene ones, with particles sizing 1-2 μm and smaller.

The specific surface per unit volume of the mineral matter, owing to its progressive disintegration, is seen to drastically increase, which makes the sorption-desorption processes play a more important role. The enhanced role of sorption processes is favored by the specific crystal structure of hypergene silicates. Between the structural elements of hypogene silicates, the electrostatic (ionic and ion-covalent) bonds are operative. In clay minerals, the electrostatic forces are operative only within a planar sheet, and the bonding between the neighbouring sheets is effected through molecular forces. Therefore the chemical elements, on their uptake by finely-dispersed clay particles, are adsorbed not only on the surface of the sheets, but can also enter the space between them. Different types of sorption processes, to mention only the cation-exchange adsorption, an essential link in the terrestrial biological cycle of chemical elements and chemosorption, play an important role in the migratory regulation

Table 4.8. Specific Surface and Capacity Characteristics for Certain Clay Minerals

Mineral	Specific surface per unit volume, m^2/g	Cation-exchange capacity, mg-eq/100 g	Overal trace element uptake, mol/g
Kaolinite	7-30	3-22	30-70
Illite	65-100	10-40	65-95
Montmorillonite	700-800	69-150	390-460

of elements in the pedosphere. The finely-dispersed mineral matter of pedosphere is an accumulator of a large number of heavy metals and other trace elements.

By virtue of their structural specificity, different clay minerals are capable of binding different amount of chemical elements. Minerals with an invariant spacing between the sheets have a limited sorptive capacity. For example, the cation-exchange capacity of kaolinite commonly is not higher than 10 mg-eq/100 g of mineral. Strongly expandable minerals with a larger intersheet spacing are capable of taking up a greater number of elements. The cation-exchange capacity of montmorillonite is ten times that of kaolinite. Hydromicas and mixed-layer minerals have the capacity for absorbing cations reaching several tens of mg-eq/100 g of solid matter (Table 4.8).

The concentration of trace elements is seen to distinctly vary among the major components of mineral matter of the soil. The smallest concentrations are typical of clastic quartz. For this reason, the trace element contents in loose sandy deposits are, as a rule, lower than those in loamy deposits. This distinction becomes more apparent in soils with a smaller reserve of unstable minerals and with a higher quartz content in the clastic mineral matter. Higher concentrations are typical of the finely-dispersed fraction with particles sizing less than 1 μm. The highest concentrations are found in mineral fractions with a large mass per unit volume ("heavy fractions").

3. In the complex process of soil formation, there occurs a systematic redistribution of chemical elements and components of mineral and organic matter. The resultant effect is the buildup of a soil profile made up of genetic horizons differing among themselves both compositionally and structurally. New minerals emerge, not unfrequently tending to form accumulations and aggregates of specific pattern.

Morphologically, the new formations are quite diversified, appearing as films, earthy masses, crusts, isolated crystals or their druses, and concretions of diverse shape and size. Their chemical and mineralogical composition is no less

heterogeneous. Represented among the soil-hypergene new formations are almost all of the mineral classes: sulfides, halogenides, oxides, nitrates, carbonates, sulfates, phosphates, and other species.

The new formations are geochemical indicators of definite biogeochemical processes occurring in soils. The presence of sulfides attests to the inhibition of aerobic microbiological activity, the occurrence of ferro-oxide tubular concretions is typical of an oxygen deficiency and availability of Fe^{2+}. Small-size globular concretions of iron and manganese hydroxides are characteristic of forest soils in the regions of cool humid climate. Diverse calcareous concretions are typical of the soils of arid landscapes. Different types of new formations contain definite trace elements: in iron hydroxides, elevated concentrations of heavy metals have been reported, and in new carbonate formations, of strontium.

In the lower soil horizons, there are occasionally found mineral formations apparently not corresponding to the biogeochemical conditions of recent soils. Thus, for example, there have been found large calcareous concretions and remnants of a powerful gypsum horizon of original acicular structure in gray-brown soils of the Central Asia. These formations are relicts of ancient hydromorphous soils preserved in the lower part of the soil of a recent desert.

4.5. Distribution of Trace Elements in Pedosphere

As has been noted earlier, the chemical composition of pedosphere is quite inhomogeneous. The relative content of most chemical elements in the soils of different regions may vary hundred and thousand times. The least variations are observed only for a small number of major elements, for example, silicon and aluminum whose relative content in the pedosphere varies by a factor of $10n$. This behaviour, established by Mitchell (1964) in his early studies of trace elements in soils, has a basically essential conceptual importance for the biogeochemistry of pedosphere.

In view of such a strong concentrational variability, the statistical treatment of analytical data becomes an issue of special concern. The acquired experience has shown that the normal (Gaussian) and lognormal distributions of analytical data quite often are violated for a certain number of samples with relatively high concentration. This leads to an overestimation of the arithmetic mean and to a significant underestimation of the geometrical mean. An adequate estimate of the concentrational level of an element in the soil of a particular locality can be obtained in terms of the modal (the most frequent) values and their mean square deviations.

Table 4.9. Metal Concentration Variation in the Soil-Forming Rocks of Karelia with Increasing Content of Argillaceous Minerals (minor elements in Karelia, 1973)

Soil-forming rock (0.001 mm fraction)	Metal and its concentration, μg/g				
	Mn	Zn	Cu	Co	Mo
Fluvio-glacial sand	353.04	12.85	7.65	3.34	0.81
Loamy moraine	650.33	18.57	14.67	5.66	1.10
Heavy-clay moraine	1475.50	19.89	31.57	10.69	1.16

Among a variety of factors affecting the modal concentrations of trace elements in the soil, the major ones are the contents of finely-dispersed minerals (fraction of particles sizing less than 0.001 mm) and organic matter. The data in Table 4.9 indicate that the concentration of heavy metals increases with higher contents of clay minerals and organic matter. The factors affecting the modal concentration of trace elements are also provincial geochemical features of the covering of soil-forming deposits and the mineral-petrographic diversity of the original rocks that serve as a source for clastic minerals contributing to the covering deposits. Important factors are also the hydrologic regimen and the intensity of soil profile washing.

The elemental concentration varies along the soil profile in a manner specific to each particular type of soil. Therefore, in characterizing the elemental concentration in the soil cover of a given locality, the reference is made to the upper humic horizon.

For the reason that most of the land is covered with the automorphous (also referred to as zonal) types of soil, the average elemental concentration in the soil cover of large regions or even of the entire land is treated in terms of the data referring to the automorphous soils.

The above remarks imply that the determination of the average elemental concentration in pedosphere is an arduous task. The first attempts were made by Vinogradov (1950), Mitchell (1955, 1964), and Swain (1955). The basic data were mainly obtained from studies of trace elements in the soils of temperate and boreal belts of the Northern Hemisphere leaving, however, out of consideration the elemental contents in the tropic soils that accounted for a larger part of the pedosphere. More detailed results were reported in the later works by Bowen (1966), Brooks (1972), and Rose *et al.* (1979). For a long time the data as gathered by Vinogradov have served for a reference for the average content of trace elements in soils.

Table 4.10. Concentration of Trace Elements in the Terrestrial Soil Cover

Element	Soils of the USA (after Shacklette *et al.* 1984)					Soils of the World (Vinogradov 1957), arithmetic mean, mg/g
	number of samples analyzed	arithmetic mean, μg/g	value range, μg/g	geometric mean, μg/g	rounded-off modal value, μg/g	
Ti	1317	2900	70–200000	2400	2800	4600
Ba	1319	580	10–5000	440	600	500
Mn	1317	550	< 2–7000	330	500	850
F	1045	430	< 10–3700	210	400	200
Zr	1319	230	< 20–2000	180	175	300
Sr	1318	240	< 5–3000	120	180	300
V	1319	80	< 7–500	58	70	100
Rb	355	67	< 20–210	58	70	100
Zn	1248	60	< 5–2900	48	58	50
Cr	1319	54	1–2000	37	40	200
La	1293	37	< 30–200	30	30	40
B	1319	33	< 20–300	26	30	10
Y	1319	25	< 10–200	21	26	50
Cu	1311	25	< 1–700	17	20	20
Li	1258	24	< 5–140	20	22	30
Ni	1318	19	< 5–700	13	17	40
Pb	1319	19	< 10–700	16	16	10
Ga	1316	17	< 5–70	13	15	30
Nb	1269	11	< 10–100	9.3	10	—
Th	297	9.4	2.2–131	8.6	9.5	6
Sc	304	8.9	< 5–50	7.5	9	7
Co	1311	9.1	< 3–70	6.7	8	8

As	1257	7.2	< 0.1–97	5.2	6.5	5
Yb	1250	3.1	< 1–50	2.6	3	—
U	354	2.7	0.29–11	2.3	2.8	1
Sn	355	1.3	< 0.1–10	0.89	1.1	10
Ge	355	1.2	< 0.1–2.5	1.2	1.4	—
I	399	1.2	< 0.5–9.6	0.75	1.4	5
Mo	1298	0.97	< 3–15	0.59	3	2
Be	1303	0.92	< 1–15	0.63	—	6
Br	348	0.85	< 0.1–11	0.56	0.8	5
Sb	354	0.66	< 1–8.8	0.48	1	1
Se	1267	0.39	< 0.1–4.3	0.26	0.36	0.01
Hg	1267	0.09	< 0.01–4.6	0.058	0.051	0.03

The determination of average concentrations for definite mineral-geochemical may refer to the results on elemental contents in the soil cover of the USA territory as reported by Shacklette and Boerngen (1984); these are summarized in Table 4.10.

Given in Table 4.10 are the arithmetic means and geometric means of elemental concentrations as estimated by a large number of samples analyzed, the limiting concentrations, as well as the rounded-off modal values estimated by us. A comparison of the modal elemental concentrations in the USA soils with the data for the world soils reveals that the latter data reflect merely the order of modal values. The fact does not come as a surprise considering the effect of a variety of factors and, accordingly, the appreciable concentrational variation in different soils. The data in Table 4.10 indicate that the concentration of many elements in the USA soils is varied within a range of $n\,100$-$n\,1000$. The least variational amplitude, about $n\,10$ is typical of the elements tightly held in the mineral matter of soil and weakly differentiated between the clastic and finely-dispersed mineral components. Such are Th, Rb, Li, B, La, Y, and Yb. It should be recalled, that the same elements are poorly taken up by plants and exhibit the K_b smaller than 1.

It is noteworthy, that Shacklette and Boerngen have established a difference in the concentrational levels of trace elements in the soil cover eastward and westward of the 96° W longitude meridian. In the soil cover of the eastern USA, higher concentrational levels have been reported for zirconium, rubidium, and niobium, whereas in the western regions, higher concentrations are typical of heavy metals and their congeners. In these findings resides the provincial geochemical distinction between the loose covering deposits and the soils evolved therefrom of the eastern and western territories. In the mineral matter of soil cover of the eastern territories, the material originating in a long-term evolution of the Precambrian basement rocks is predominant. The influence due to the original rocks with clearly defined metallogenic specialization is traced back in the metal content of the western territory soils.

In the course of interaction between the living matter of land and the mineral substrate, the soil depth differentiates into genetic horizons constituting, in their entirety, the soil profile. The profile structure and the composition of genetic horizons differ from soil to soil. Accordingly, the distribution of chemical elements along the soil profile is also different.

Given in Table 4.11 are the relative contents of Cu, Pb, and Zn in the widespread soils of the southern part of the West-Siberian low plain. It will be observed that the concentration of the three metals varies in an orderly manner along the profile of sward-podzolic soil, whereas in the chernozem there occurs a gradual concentration decrease down the soil profile. This should be attributed to a substantial distinction of the biogeochemical processes occurring in the considered soils.

Table 4.11. Variation of Heavy Metal Concentration down the Profile of the Soils of Zapadno-Sibirskaya Ravnina (after Izerskaya 1979)

Soil and soil horizons	Metal and its concentration, mg/kg		
	Cu	Pb	Zn
Sward-podzolic soil			
A_1	14.1	25.4	42.6
A_2	10.8	20.4	32.1
B	21.2	30.7	47.6
C	18.4	26.0	45.8
Grey forest soil			
A_1	21.2	27.3	41.4
A_1/A_2	18.9	22.6	35.3
B	22.7	25.4	45.0
C	19.5	23.2	40.6
Chernozem			
A	26.0	35.2	43.2
A/B	24.6	32.3	37.8
B	19.6	33.5	37.7
C	21.7	31.5	38.3

In the soils in question, the metal content in the uppermost A_1 horizon is greater than in the horizon situated below. This difference should be attributed to the occurrence in the A_1 horizon of plant remains acting as accumulators for the metals taken up by the plants. The transformation of organic matter in sward-podzolic soils and chernozems is basically different. In the former, the plant remains decompose to yield fulvic acids which are readily soluble in water and provide for the acid soil reaction. Fulvic acids accept metals to form intracomplex compounds which are washed out of the upper part of the soil profile. The percolating acid waters also carry from the upper profile of sward-podzolic soils finely-dispersed particles which are deposited in the illuvial B horizon. In the same horizon, iron hydroxides become deposited forming thin films and clumps of amorphous matter on the minerals. Clay particles and iron hydroxides are effective sorbents for metals, which makes the metal concentration increase in the B horizon.

The biogeochemical processes in the chernozem soils are entirely different in character. Here, the decayed plant remains yield humic acids and humates insoluble in water. These species form gels which agglutinate the dispersed particles into water-resistant aggregates preventing thereby the particle transport

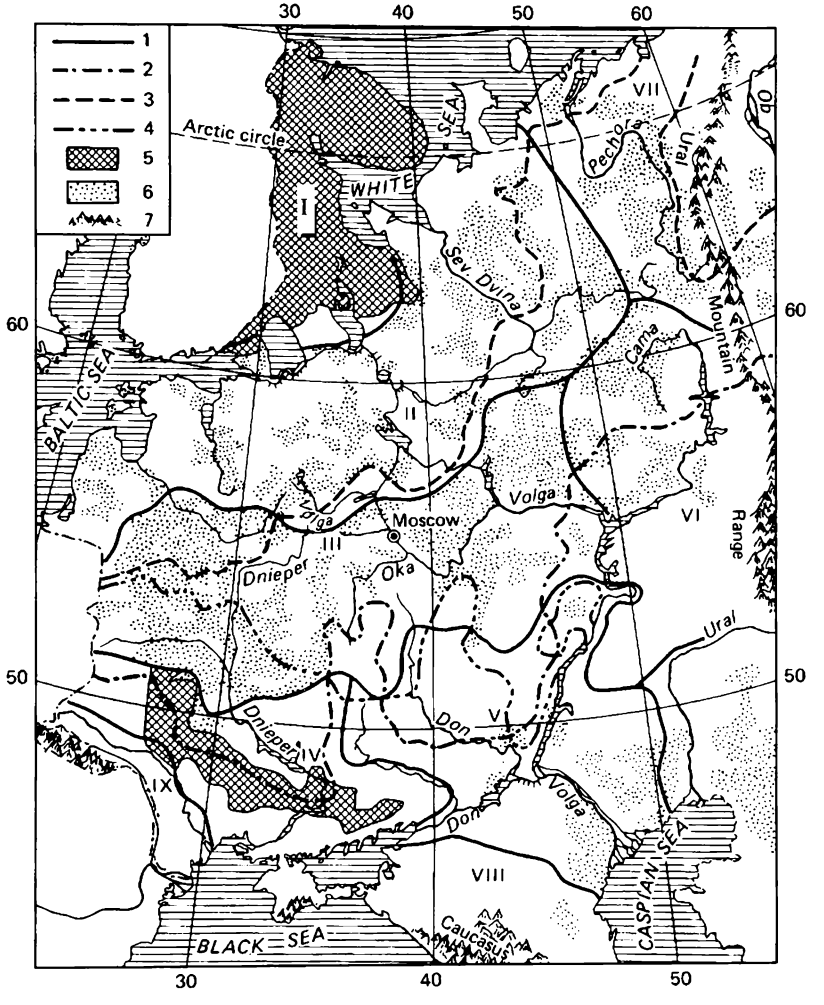
by percolating soil waters. Humic acids, by virtue of their ability to form stable complexes with metals, prevent the metal wash-out. For this reason, the concentration of metals and other trace elements in the chernozems is higher than in the sward-podzolic soils. The humic acid concentration decreases gradually down the soil profile; accordingly, the metal concentration also decreases.

Without going into details about the biogeochemical processes in gray forest soils, we restrict ourselves to a remark that the metal distribution along their soil profile takes an intermediate place between the distributions for the sward-podzolic soil and the chernozem.

The profile distribution of the overall metal contents gives a grossly generalized pattern for the distribution of different forms of metals in the soil. A study of the copper forms in the sward-podzolic soils of the central Russian plain has shown that water-soluble forms account for 0.1-0.9% of the overall copper content; exchangeably adsorbed forms, for 0.7 to 3.9%; tightly adsorbed forms, for 7 to 24%, and iron hydroxide-bound forms, for 40 to 55%. The organic matter of the humic A_1 horizon contains 24 to 36% of the copper total found in this horizon (Zhuravleva 1973). A significant part of trace elements is tightly held by the finely-dispersed clay minerals. For this reason, the relative metal content in loamy soils is 2-3 times higher than that in sandy soils rich in clastic quartz.

The elevated concentration of trace elements in the upper humic soil horizon is associated with the uptake of elements by plants and their supply to the soil in the decayed plant organs. The elemental concentration in the lower horizon is determined by their content in the soil-forming substrate (loose covering deposits). The soil-forming substrate is made up of intermingled components of local original rocks and the allochthonous material carried in by surface waters or by the wind. Thus, the covering deposit composition reflects an integrated mineralogical composition of the original rocks of a more or less large region. For this reason, the covering deposits and the mineral matter of soils reveal distinctly the provincial features of mineral composition for definite territories. By virtue of the fact that the minerals are hosts for trace elements, the levels of trace elements contained in the mineral matter of soils from various regions differ among themselves. For example, the contents of titanium, vanadium, copper, lead, and molybdenum are elevated in the loose pleistocene depositions covering the Kazakh hercyan platform. In the soil-forming rocks and the mineral matter of soils of the Russian plain, the zirconium content is elevated, whereas in the soils of the Priural'e, higher concentrations are observed for nickel, cobalt, and copper (see the map below).

Still more clear-cut features appear to be in the provincial geochemical features of soils in the tropic. This is associated with the fact that a larger part of the tropical land is devoid of the heavy cover of allochthonous-glacial



Mineralogical provinces of quarternary covering deposits of the European part of the Russian Federation

I—Kol'sko-Karel'skaya province; *II*—Pribaltiisko-Arkhangel'skaya pr.; *III*—Tsentral'no-Russkaya pr.; *IV*—Ukrainskaya pr.; *V*—Volzhsko-Donskaya pr.; *VI*—Priural'skaya pr.; *VII*—Zatiminskaya pr.; *VIII*—Predkavkazskaya pr.; *IX*—Predkarpatskaya pr.; (*1*) province boundaries; (*2*) glacial boundary; (*3*) 1st upper quarternary glaciation boundary; (*4*) northern boundary for massive tertiary deposits; (*5*) conterminate areas of crystalline rocks; (*6*) areas of high quartz concentration and low level of trace elements; (*7*) mountains

or aeolian (loessal) material. The loose red covering deposits of the Pliocene-Pleistocene epoch serve for a soil-forming substrate. In these deposits and the soils evolved from soils in the volcanic region of the north-eastern Tanzania, elevated contents of beryllium, yttrium, lanthanum, niobium, and zirconium have been found. Chromium and vanadium occur in higher concentration in similar deposits overlying the precambrian crystalline rocks of the Ugandian plateau.

As a result of the regular changes in content and proportion of the host minerals for trace elements, geochemical mineral provinces have evolved in the covering deposits and the pedosphere. Different concentrational levels of trace elements in various territories affect the capacity of mass-exchange biogeochemical cycles of these elements.

The varied content of trace elements in the loose covering deposits manifests itself both across a large territory as weakly contrasted provincial differentiations and within a limited area, strongly contrasted, as geochemical anomalies.

The degradation of near-surface ores is accompanied by an extensive dispersal of metals. Around the ore-body outcrops, the so-called halos of dispersion are formed. The covering deposits as formed in the course of relief planation, are composed of a mixture of local components and of variable amounts of the allochthonous material. They give rise to irregular, more or less isometrically contoured halos. Their specific feature is a rapid surfaceward concentrational depletion of dispersed elements and a contraction of the area of dispersion halo from the ore body toward the surface. Lean deposits, with the compositional dominance of clastic local materials, are favorable for the formation of open, that is, surface-exposed halos (see Fig. 13A).

In deposits with the dominance of allochthonous components, inhibited, poorly expressed halos are formed (Fig. 13B). An interruption in deposition and the augmentation of allochthonous material are favorable to the shielding of a geochemical anomaly and to the buildup of a buried halo of dispersion, not exposed to the surface.

The interactions between vegetation, edaphic biota and mineral substrate facilitate the formation of geochemical anomalies on the soil surface. The metals, dispersed from an ore body, accumulate in the forest litter, whereas their concentration in the elluvial horizon and in the soil-forming rock is indistinguishable from the local "geochemical background". In this particular case, as was aptly observed by Goldschmidt (1938), the tree vegetation performs the function of a geochemical pump that delivers the ore elements from the depth to the surface. A geochemical anomaly in the forest litter or in the humic horizon can be more pronounced than a biogeochemical anomaly in the plants.

The surface sampling from soils and loose deposits followed by an analysis for metal content with a view of prospecting for ore deposits has been named the metallometry. Starting from the late 1940s, metallometry has rapidly gained a worldwide popularity. The metallometric method has proved helpful in

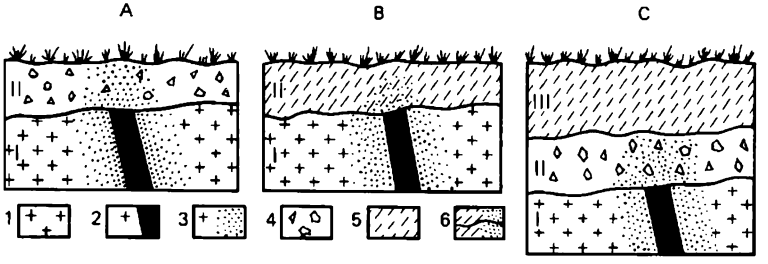


Fig. 13. Schematic pictures of the secondary dispersion halo in covering deposits

A—open halo; *B*—suppressed halo; *C*—buried halo; *1*—basic rock; *2*—ore body; *3*—endogenic dispersion halo; *4*—eluvial-deluvial covering deposits; *5*—loess; *6*—elevated concentration region for dispersed ore elements in the covering deposits

discovering large ore deposits of tin, tungsten, molybdenum, zinc, lead, and other metals.

It should be pointed out that the high differentiation of a soil profile creates some difficulty for the application of metallometry. The interpretation of analytical results may prove to be a very complicated task if the sampling has been made without due account of the geochemical specificity of genetic horizons. For this reason, the metallometric prospecting on territories with highly differentiated soil profile (for example, podzolic soils) should be carried out in its pedological-geochemical modification.

The effectiveness of ore prospecting can be further enhanced if soil-specific forms for the metal occurrence are considered, rather than the overall metal content. It has been noted earlier that the interaction of living organisms with the mineral matter of the soil yields complexes of metals with specific organic compounds; such complexes are sparingly soluble in water, but are amenable to their separation by special extractions. Consequently, through performing an analysis not for the total metal content in the soil, but rather for metal content in organic compounds extractable with acid-alkaline solvents, one may take the chance to identify a latent pedo-geochemical anomaly potentially indicative of a deep ore deposit (Dobrovolsky 1964). Since the concentration of trace metals complexed with organics is very low in the soil, Antropova (1975) suggested to use the metal-to-humic carbon ratio rather than to refer the analytical value to the soil mass. This approach has proved to be quite fruitful.

Owing to its high sorptive capacity, the peat material becomes enriched in metals from the groundwaters in contact with ores of shallow bedding. The Finnish geologist Salmi (1963) took advantage of this effect and proposed a method for ore prospecting via analysis of peat. He found geochemical anomalies of copper, lead, zinc, vanadium, and titanium in peatlands in close vicinity of ore bodies overlaid with glacial deposits 10 to 12 m deep.

The above examples show that the concentrational variation of metals and other trace elements in the World's land surface showing up as pedological-geochemical provinces and soil anomalies is a widespread effect. It may be presumed therefore that the concentrational variability of trace elements which are important physiological factors has played a role in the evolution of terrestrial life and its highly diversified forms.

4.6. Epochal Relicts of Ancient Soil Formation

The processes of interaction between the mineral matter of Earth's crust and the living matter of land developed continually with the general evolution of the organic kingdom and terrestrial forms of life. The ancient soil formation, in principle adequate to the recent, could evolve as a sustained process only with the appearance of a primordial terrestrial vegetation, the psilophyte flora at the late Silurian (410-420 million years). Concurrently, the edaphic fauna evolved. In particular, the Devonian soils provided a habitat for crustaceous ticks. The ticks constitute a widely occurring invertebrate group in the recent soil of humid landscapes, with their population reaching 40-100 thousand species per square meter. There have been reported fossil records of crustaceous ticks dating back to a more remote period, in the Cambrian deposits (D.A. Krivolutsky, personal communication). Most fossil crustaceous ticks were in all probability confined to the organic remnants of boggy deposits.

Long in advance of the appearance of terrestrial plants and edaphic invertebrates, the land was a repository of continually accumulating organic matter. The major contributors to this process were cyano bacterial communities in aquatic landscapes. Shungites of the Upper Proterozoic, occurring in the south-eastern Karelia, appear to be accumulations of this type.

The rock remnants involved in the most ancient hypergene processes go back for 2-2.5 billion years. In further course, those formations underwent metamorphism and recrystallization, which poses difficulties in their detailed study. The only forms of terrestrial life that thrived at those times were bacteria. Although our knowledge of that period cannot allow but of a parsimonious conclusion, the idea of ancient "bacterial soil formation" deserves a cursory consideration at least.

Starting from the Upper Paleozoic, one may attempt to distinguish several epochs for the profound pedo-hypergene transformation of rock matter and for the formation of soil profiles composed of the horizons of a continuous gradation of hypogene silicates to hypergene clay minerals. Such profiles have been named the crusts of weathering. Their buildup fell into periods of a long-lasted biostasy of humid forest phytocenoces. During the subsequent periods of rhexistasy and rapid erosion, the crusts of weathering suffered degradation,

and their mineral components made part of the sedimentary deposit composition. The best preserved were the ancient crusts formed in the Upper Mesozoic. They were spread over the extensive fragmental areas of the ancient Gondwana protocontinent as well as in separate regions of the extratropical World's land.

The types of weathering crusts are quite diversified, which should be attributed to the compositional diversity of original rocks and to the varied conditions for their formation. Elluvial (automorphous) and hydromorphous crusts are distinguished. The automorphous crusts were formed on the positive relief elements by the action of percolating soil waters. The uppermost horizon in which organic matter was being accumulated failed to be preserved. The hydromorphous crusts were formed on essentially negative elements, under the conditions of close vicinity to the permanent or seasonal groundwaters from which accumulations of chemical elements were profusely deposited.

The massive crusts that resulted from a long-lasted (millions of years) hypergene transformation of granitoids and metamorphic rocks, exhibit a white, intensely leached-out horizon in the upper part of soil profile. It is composed of kaolinite or metahalloysite as well as residual quartz, depending on an occasional occurrence of the latter in the original rock. In this case, the law of convergence for the end products of pedo-hypergene transformation comes into play: irrespective of the compositional diversity of a large group of original rocks, the upper profile horizon has a close composition specifically devoid of most trace elements.

Table 4.12 provides data for the kaolinite horizon of two crusts of weathering, both of the same Upper Mesozoic age, but originating in regions distant from each other: Uganda (East Africa) and the Ural Mountains (USSR). Both objects exhibit clarkes of concentration seldom greater over 1 for most trace elements. Vis-à-vis this general trend, specific provincial geochemical features inherent in the original rocks become apparent. In particular, the Uralian crust contains more copper, nickel, and cobalt; as distinct, the Ugandian crust is more abundant in niobium and gallium.

The profile buildup in the crusts of weathering of ultrabasic rocks proceeds with a concentrational increase of certain trace elements, especially nickel, cobalt, and chromium. Such an effect has been established in the well-studied crusts of weathering for hyperbasites of New Caledonia, Cuba, and the USSR (the Ural Mountains).

In the relatively negative relief elements, the pedo-hypergene processes were subject to permanent or seasonal action by the groundwaters of a close neighbourhood from which definite chemical elements were systematically deposited. Therefore, in forming the hydromorphic crusts, a major role was assigned not to the elemental loss, but to its exact opposite, the accumulation of trace elements which were carried out of eluvial crusts. The geochemical conjugation effect which has been discussed earlier in comparing the concen-

Table 4.12. Content and Clarke of Concentration of Trace Elements in the Kaolinitic Horizon of the Ancient Crust of Weathering (Dobrovolsky 1983)

Element	Uganda		The Southern Urals	
	content, $1 \cdot 10^{-4}$%	clarke of concentration	content, $1 \cdot 10^{-4}$%	clarke of concentration
Ti	2700	0.6	4970	1.1
Mn	18	0.1	406	0.4
V	78	0.5	105	0.8
Cr	100	1.0	32	0.3
Ni	26	0.3	37	0.5
Co	10	0.4	13	0.5
Cu	9	0.4	41	0.8
Pb	18	1.4	34	2.6
Zn	70	1.0	53	0.8
Sc	14	0.6	15	0.7
Nb	30	1.5	nil	nil
Zr	101	0.6	138	0.8
Ga	31	1.9	27	1.8
Ba	45	0.1	75	0.2

tration of heavy metals in the peat of raised bogs and lowland bogs likewise manifests itself in the compositional proportion of eluvial and hydromorphic crusts.

To exemplify a hydromorphic crust, one may refer to the laterite armours which are widely spread in tropical territories. Owing to hydrogen accumulation, the concentration of actively migrating elements (copper, zinc, vanadium, chromium, and others) in the laterite armors is higher by an order of magnitude than in the eluvial crusts from where the trace metals have been eliminated.

A comparative study of the ancient crusts of weathering and the recent soils of equatorial African landscapes (Dobrovolsky 1973, 1974) has shown that the ancient and recent pedo-hypergene processes tend in the same direction. Simultaneously, the transformation of mineral matter in the profile of ancient crustal soils was, beyond comparison, more intense than in the recent soils. Presumably, this may be due to a very significant evolutionary period (millions of years) of the ancient epochs of biostasy and the associated therewith biogeochemical action on the original rocks as distinct from the geologically short lifetime of modern soils.

4.7. Equilibria in Biolatent Soil System

The performance of a multicomponent soil system is based on a continuous exchange of matter and energy between its components. The mass exchange of chemical elements is maintained by a variety of intercomponent equilibria among which a special emphasis should be placed on the equilibria between the solid and liquid phases of the soil. This is due to the fact that precisely the soil solutions are suppliers of elements required by higher plants for the synthesis of their annual production. Simultaneously, the soil solutions serve as a nutritional medium for the microorganisms whose major function is digestion of dead organic matter. Thus, the soil solutions play a major role in the mechanism of biogeochemical cycles involving the mass exchange of chemical elements.

The concentration of elements in a soil solution is maintained at a definite level owing to the equilibrium between elements in the liquid and solid phases of the soil. The equilibrium distribution of elements between these two phases is determined by the processes of precipitation-dissolution and adsorption-desorption.

A compound, capable of dissolving in water, becomes exposed, on its supply to the soil, to the action by H^+, OH^-, CO_3^{2-}, HCO_3^-, $H_2PO_4^-$ ions, water-soluble humic acids and other agents. At the same time, the interaction between solution and solid phase of the soil is accompanied by the concentrational decrease of trace elements in solution. Sequentially performed aqueous extractions with a soil sample yield little varied metal concentrations in the extraction solution implying thereby that the metals, contained in the solid phase and in solution, are at equilibrium.

According to the theory of chemical equilibrium, the composition of an equilibrated solution is controlled by a process involving the least elemental concentration in solution. Vorob'eva *et al.* (1980) have argued that the precipitation-dissolution process in which the least soluble compound takes part is of prime importance. These authors believe, first, that the natural solutions are saturated with respect to the least soluble metal compounds which are at equilibrium with the solid phase of the soil. This hypothesis lends support in the fact that in multiple repeated sequential extractions and in the overall extraction of a metal from a soil sample, the metal concentration in the extraction solutions remains practically the same. Second, in accordance with the Le Chatelier principle, the concentrational level in the solution must be limited by the compound which, under the given conditions, deposits a precipitate at its least concentration.

The phosphate ions are species which form with heavy metals the least water-soluble compounds. Therefore, the presence of phosphates must be a deter-

Table 4.13. Concentration of Lead in the Solid Phase and the Aqueous Extracts of Soils (after Lobanova 1983)

Soil and its horizons	Overall Pb concentration, mg/kg	Pb phosphate concentration, mg/kg	Pb concentration in aqueous extract, μg/l
Sward-podzolic soil			
A_1	16.5	1.0	2.5
A_2	9.0	0.6	1.7
B_1	13.0	0.7	1.2
Typical deep chernozem			
A_1	25.0	1.0	1.5
B_1	22.5	0.7	1.0
C	22.5	0.7	1.0
Brown mountain forest soil			
A_1	42.0	4.0	2.5
B_1	27.0	3.0	1.5
B_2	33.0	3.0	1.0

mining factor for the concentration of heavy metals in soil solutions and in aqueous extraction solutions. The metal phosphates contained in the solid phase of the soil may be regarded as a reserve for maintaining the metal concentrations in the soil solution. As an example, Table 4.13 presents the overall content of lead, the content of lead phosphates, and the concentration of lead in extraction solution as obtained for different types of soil.

In view of the negligible content of phosphate ions in soil solution, the available phosphates do not suffice to precipitate all of the dissolved metals. At the same time, with the solid soil matter added to aqueous extraction solutions, the concentration of heavy metals lowers rapidly owing to adsorption. In this particular case, the adsorption is meant to indicate a variety of ways to remove heavy metals through binding them to the solid matter with no formation of individual chemical species.

Experimental data on adsorption of heavy metals and their congeners by a solid phase from solution are satisfactorily treated by the Freindlich equation of adsorption isotherm

$$x/m = K \cdot C^{1/n}$$

where x/m is the amount of metal adsorbed, C is the equilibrium concentration of metal in solution, K and n are constants.

The results as obtained by various authors have shown that two branches are distinguished in the isotherm for metal adsorption: the first branch is inclined at a large angle to the abscissa axis, while the second branch is less steep. Such a course of the isotherm curve is explained by the fact that, at low concentration in solution, the heavy metal ions primarily compete for high-energy sites on the solid surface (specific adsorption of metals by soil); all of those sites having been occupied, the metal ions proceed with binding to lower-energy sites (nonspecific adsorption). The specifically adsorbed cations are held to the solid phase of the soil mostly through covalent or coordination bonds, whereas the nonspecifically adsorbed, are held through ion-exchange bonds.

The specific adsorption involves the humus and protonated iron hydroxides, these latter spreading as very thin films on the surface of clay particles. Gorbatov (1983) in his experiments using the method of Mehra and Jackson (1960) for the destruction of humus by hydrogen peroxide and the removal of iron hydroxide films has shown that the chernozem, thus treated, took up twice as less lead and 10% as less zinc. The specific adsorption of heavy metals is selective: Pb > Zn > Cd. Lead becomes preferably linked to Fe(III) hydroxides, and zinc, to humus. About one third part of zinc and a larger part of cadmium persist in a cation-exchange form (see Table 4.14).

Complexes of metals with humic matter and Fe(III) hydroxides are quite stable. Likewise stable are chemisorbed species bound via molecular forces. Metals that persist in the cation-exchange form are the easiest to pass into solution. Consequently, as more of metal is adsorbed by organic matter, the larger part of it remains fixed in the soil. By contrast, the more metal persists in the cation-exchange form, the greater part of it is amenable to easy mobilization. Of the three metals represented in Table 4.14, the most mobile is cadmium, and the least mobile, lead. Metals, tightly held by the organic matter, are inaccessible to plants. For this reason, plants that grow on drained swampy soils rich in poorly decayed organic matter which is high in copper, zinc and manganese suffer not infrequently from a physiological deficiency in these metals.

The cation-exchange adsorption is mainly associated with finely-dispersed clay minerals. Along with this form, some metals are held more tightly in clay minerals, presumably owing to their penetration into the intersheet spaces of crystal structure of these minerals.

The adsorption of trace elements and the equilibrium between the solid and liquid phases of the soil play an important role in the supply of these elements to plants. As is known, there are two routes for the supply of elements to plants (Rubin 1976). The first route is the active uptake of an element by the cell against the concentration gradient, and the second route, is the passive transport along the gradient. The active uptake requires an expenditure of energy and is, as a rule, a selective process associated with the biogeochemical

differentiation of elements (see Section 1.3). The passive uptake is effected in parallel to transpiration.

The type of supply of an element to the plants is dependent on the concentration of the element in soil solution. At low concentrations, which are typical of trace elements under the "geochemical background" conditions, the active selective uptake of elements by plants is of prime importance. If an element, commonly occurring in negligibly small amounts, is present in the soil solution at an abnormally high concentration, it is supplied to the plant by passive transport. Dewit and Verbeken (1978) found that the supply of cadmium to wheat at a concentration of the element in solution lower than 0.5 mg/l was regulated by the membrane processes; at higher concentrations, the supply became switched to a passive transport.

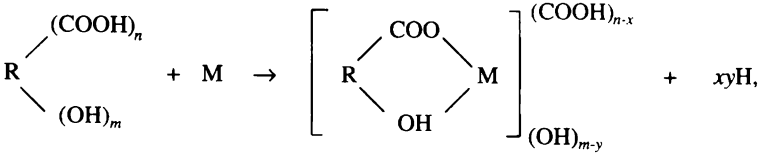
The soil, owing to its significant sorptive capacity and to the effects arising from the above equilibria, exhibits a remarkable ability to bind excess heavy metals and to maintain their concentration in soil solution at a low level providing for the selective uptake of needed amounts of metals. If the soil solution becomes deficient in a metal, the soil is capable of supplying an additional amount of the metal owing to the equilibrium between the solid and liquid phases.

Metals, on their uptake by humus, bind most actively to carboxyl (COOH) and phenolic hydroxyl (OH) groups through replacing the hydrogen atom, whereby chelates are formed with a metal making part of the anionic moiety of the organic molecule. According to Aleksandrova (1967), the ligated metal is engaged in coordination (homeopolar) bonding and its cationic function is

Table 4.14. The Adsorption Types for Heavy Metals in the Chernozem and Brown Forest Soil (compiled after the data as reported by Gorbatov (1983))

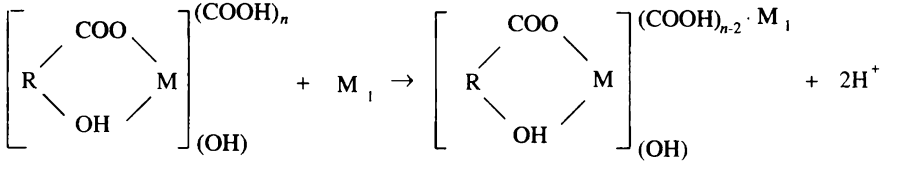
Soil and metals	Adsorption type (% of the total metal uptake)		
	cation-exchange	humic uptake	uptake by hydrated Fe(III) oxides
Chernozem			
Zn	15.6	19.4	50.0
Pb	0.9	40.0	40.0
Cd	76.2	9.5	16.2
Brown forest soil			
Zn	35.5	28.0	26.7
Pb	3.7	63.8	26.2
Cd	71.1	11.1	26.7

inhibited. A scheme for metal complexation is shown below:



where M = $Fe(OH)_2^+$ or $Fe(OH)^{2+}$.

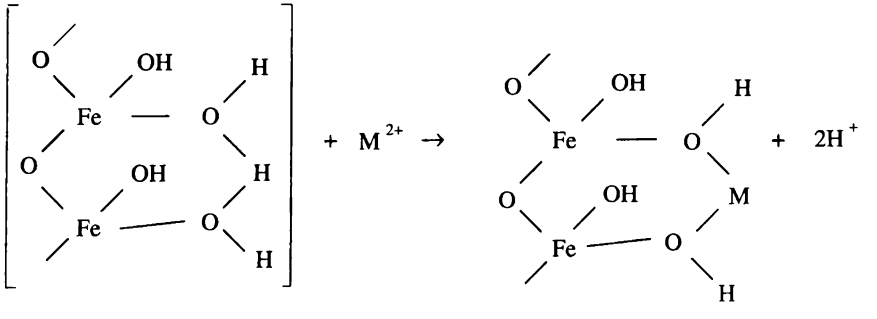
The complex can add a metal in exchange for H^+ in the outer-sphere functional groups:



where M_1 is a bivalent metal cation.

Therefore, the metal can make part of both the anionic and cationic moieties of the humic acid molecule. As has been noted in Section 4.3, the molecules of humic compounds from various soils differ in the number of functional groups and in the extent to which the "core" is fused. For this reason, the metal uptake is influenced not only by the nature of the metal, but also by the structural specificity of humic compounds.

The interaction of metals and Fe(III) hydroxides is effected through binding a metal ion to two OH^- groups. The scheme below is suggestive of the probable interaction of the metal with X-ray-amorphous Fe(III) hydroxide with a hydrohoetitte-type composition:



Proper concentrational levels of trace elements in soil solution are exceptionally important for the normal biotic activity of plants. In the course of evolution, the plants have developed mechanisms for blocking excess trace elements, primarily, heavy metals.

Il'in and Stepanova (1980) have hypothesized that trace elements can, to some extent, be prevented from entering the peripheral roots in the vicinity of the Casparian strip. Presumably, physiological mechanisms are operative to protect the reproductive organs. However, the protecting potential of plants against metal invasion is rather limited or even lacking vis-à-vis certain elements, for example, zinc (Bansal *et al.* 1982). The low concentration of heavy metals needed by plants is mainly provided for by equilibria between the solid and liquid phases of the soil.

The complexing of metals to the organic matter of the soil facilitates the long-term removal of excess metals from the migration cycles. The strength of fixation of metals in the organic soil matter is varied. The most tightly held is mercury, followed in the order of decreasing strength by lead, copper, zinc, and cadmium. Through uptake and binding of excess trace elements as supplied in an active soluble form to the land surface, the pedosphere performs the function of a global accumulator for trace elements, with the organic matter playing a pivotal role.

The trace element concentration in soil solutions is an essential factor for normal activity not only of higher plants, but also of edaphic microbiota. The available data provide evidence that the edaphic microorganisms are adapted to variable concentrational levels of zinc, copper, lead, cadmium, molybdenum, cobalt, and other trace elements. Starting from this evidence, Koval'sky (1974) has advanced an idea that there exist in the soils varietal ecological types of the same species of microorganisms well-adapted to definite levels of trace elements.

Letunova (1978) has studied the microorganisms inhabiting the soils of the Sumsarsky lead-zinc ore deposit and established that the most resistant to excess heavy metals are fungi, and the least resistant are bacteria. Simultaneously, the highest zinc content has been found in spore-forming bacteria (5154.1 mg/kg of dry bacterial matter), followed by actinomyces (up to 483.7 mg/kg), fungi (251.0 mg/kg), and nonspore-forming bacteria (up to 118.0 mg/kg). For lead, the order is spore-forming bacteria (1466.7 mg/kg), nonspore-forming bacteria (up to 246.7 mg/kg), actinomyces (101.7 mg/kg), and fungi (96.4 mg/kg).

The ability to accumulate metals appears to be a characteristic biogeochemical feature of soil bacteria. Probably, they are capable of producing enzymes for conversion of water-soluble metal compounds to inactive forms inside the cell. Anyway, the bacterial activity has resulted in the formation of large ore deposits of iron, manganese, copper, vanadium, uranium, and other metals. The ability of bacteria to accumulate metals was used in developing processes for micro-

biological extraction of metals from lean ores and for microbiological disposal of waste waters.

Despite their ability to accumulate metals, the microorganisms that thrive in soils with normal, moderately low metal concentration, are very responsive to an increase in metal concentration. This manifests itself in the inhibition of biogeochemical activity of certain groups of organisms, in particular, nitrogen-fixing bacteria.

The experiments of Letunova (1978) with soil extracts and *in situ* microbiological study of edaphic microorganisms have shown that the nitrogen-fixing bacteria *Azotobacter chroococum* from soils of different regions are adapted to varied copper concentrations. The azotobacter from the soils of the Podmoskov'e (Moscow suburban area) thrives at low concentrations of copper and molybdenum, and that from the soils of Uzbekistan (Central Asia), at much higher concentrations. The addition of more copper and molybdenum to a Podmoskov'e soil extract inhibited the growth and nitrogen fixation of the bacterial strain, whereas the same metal concentration produced no effect on the azotobacter from the Uzbekistan soil.

Umarov *et al.* (1980) have established that excess cadmium produces the strongest inhibitory effect on the nitrogen-fixing activity of the soil, the effect by copper is less intense, whereas lead is the least active inhibitor. Presumably, the extent of metal toxicity is related to the strength of metal adsorption by the solid phase of the soil following the order Pb > Cu > Cd. The inhibitory effect of nitrogen-fixing activity of soil by excess metal doses to which the microorganisms are ill-adapted may be used for assessing the technogenic contamination of soils.

5 Global Biogeochemical Cycles and Distribution of Chemical Elements in the Biosphere of the World's Land

As follows from the foregoing material, there exists in the biosphere an intimate relation between the chemical compositions of the Earth's crust, World's ocean, and atmosphere. This relation is determined not only by the coexistence of solid, liquid and gaseous matter on the planet surface, but also by the mass exchange between the outer Earth's shells that have evolved during 4 billion years of the geological history of the Earth.

In essence, the mass-exchange processes are manifestations of the equilibria between global heterophase accumulations of matter in the planet's periphery. These processes were inherently cyclic in character owing to diurnal, annual, and more extended fluctuations of the energy supplied by the sun. The mass-exchange cycles were not invariable, and their changes in one or another direction entailed changes in the composition of interdependent Earth's shells.

The living matter was a major factor which affected both the global mass-exchange cycles and the initial system of phase shells and which finally led to the emergence of extant biosphere. Living organisms involved in the system of cycles to perform essentially the same functions as those of abiogenous chemical systems, produced metabolites and died off at the end of their life cycle. The accumulation of dead remnants during an extended period of time brought about changes in the environmental geochemical conditions which, in turn, forced the living organisms into adapting to the newly-arisen surroundings.

Initially, the biotic activity was confined to local conditions, which presumably might be hydrothermal conditions (Brock 1978) or to hydrospheric conditions in the presence of free oxygen (Claud 1980). In further course, life expanded over the entire surface layer of the ocean and then spread to the land. The concurrent processes were "biogenization" of global cycles and their structural diversification.

The functional individualization of chemical elements in the biogeochemical cycles has profoundly affected the compositions of sedimentary shell, World's Ocean, and atmosphere. Life was shaping the habitat through a continuous cyclic mass exchange. A most striking example is the buildup of the pedosphere which has originated in the activity of terrestrial biota and which has simultaneously provided for the existence and reproduction of a major part of Earth's biomass, the World's land vegetation.

The global mass-exchange cycles should not be regarded as circular processes confined within an inaccessible space. A better analogy would be material vortices irrevocably interwoven with their surroundings. The most daring imagination will fail to embrace the huge masses of atoms that incessantly enter and leave the migratory fluxes. It is precisely owing to their openness that the biogeochemical cycles redistribute in an orderly manner the masses of chemical elements and facilitate thereby a directional change in the composition of outer Earth's shells.

Calculations of the mass distribution for chemical elements in the biosphere and for those involved in biogenous migration are based on two groups of data. First, one must have data on the average elemental concentrations in biosphere components such as the World's land vegetation, stream waters, pedosphere, and others. Second, there must be available data on the mass of each of the biosphere components.

Currently, the data on the mass of biosphere components are very fragmentary. Still more sparse are the average concentrations of chemical elements whose precise determination meets with many difficulties, of which a major one is the wide variation of elemental concentration in particular objects of study: plant, water, and soil samples. It has been shown in the foregoing chapters that the wide-range variation of elemental content in all natural objects is a characteristic feature of the biosphere geochemistry and is determined by biogeochemical processes which, on the one hand, assist in the accumulation and, on the other hand, are actively engaged in the dispersal of chemical elements.

For these reasons, the results of calculations of the global mass-exchange cycles for chemical elements as obtained by various authors are somewhat arbitrary and not necessarily concordant, as has been noted by researchers concerned with this problem (Bolin 1972; Garrels *et al.* 1974; Walker 1980). Besides, the final estimates are strongly influenced by the starting concept adopted by a particular author.

The acquisition of novel, updated and refined information will with certainty improve our understanding of the structure of global mass-exchange cycles. Each new experience of a judicious quantitative analysis of the mass exchange in biosphere allows us to gain a deeper insight into the general picture and to outline issues requiring further attention.

The data that will be discussed in this Chapter are mainly concerned with an estimation of global mass-exchange processes occurring on the World's land. A minimum of data on World's ocean are referred to merely with a view to provide a more complete picture for the elemental mass distribution in biosphere or by way of comparison with the terrestrial processes.

The following data have been used in calculating the masses of chemical elements in the major components (reservoirs) of biosphere.

World's land

Area, $150 \cdot 10^6$ km^2
Area (excepting glaciated territories and intracontinental water bodies), $135 \cdot 10^6$ km^2
Vegetable biomass, live weight, $6.25 \cdot 10^{12}$ tons
dry weight, $2.50 \cdot 10^{12}$ tons
ash content, 5% (on a dry weight basis)
Organic matter of pedosphere
forest litter, $0.2 \cdot 10^{12}$ tons
peat accumulations, $0.5 \cdot 10^{12}$ tons
humus, $2.4 \cdot 10^{12}$ tons
total, $3.1 \cdot 10^{12}$ tons

Earth's crust

Sedimentary shell (effusives excepted), $2400 \cdot 10^{15}$ tons
Granite layer of continental block, $8200 \cdot 10^{15}$ tons
Atmosphere, $5.2 \cdot 10^{15}$ tons

Ocean

Area, $360 \cdot 10^{12}$ m^2
Volume, $1370 \cdot 10^{15}$ m^3
Biomass of photosynthetic organisms, dry weight, $3.4 \cdot 10^9$ tons
Dissolved organic matter, dry weight, $4380 \cdot 10^9$ tons

Data required for determination of mass exchange between reservoirs:

World's land

Biological turnover (photosynthesis-degradation of organic matter):
vegetation production rate (with no allowance made for human activity), $172 \cdot 10^9$ ton/year (dry biomass)
evaporation, $69 \cdot 10^{15}$ liter/year
precipitation, $114 \cdot 10^{15}$ liter/year ($44 \cdot 10^{15}$ liter/year of oceanic origin included)
transport of precipitation of oceanic origin onto land, $44 \cdot 10^{15}$ liter/year
stream flow from land to ocean, $44 \cdot 10^{15}$ liter/year ($3 \cdot 10^{15}$ liter/year from glaciers included)
suspension stream loss, $20.5 \cdot 10^9$ ton/year
soluble matter stream loss, $4.9 \cdot 10^9$ ton/year
transport of dust from land to ocean, $1.8 \cdot 10^9$ ton/year

Ocean

Biological turnover of photosynthetic organisms, $110 \cdot 10^9$ ton/year (dry weight):
evaporation, $456 \cdot 10^{15}$ liter/year
precipitation, $412 \cdot 10^{15}$ liter/year

5.1. Global Mass-Exchange Cycles for Sodium and Chlorine

The masses of chemical elements were supplied to global cycles from two sources. This becomes apparent through considering in retrospect the dynamics of existing mass-exchange cycles in the biosphere, with allowance made for the specific distribution of elemental masses in the outer Earth's shells. To this end, we wish to compare the global cycles for sodium and chlorine whose geochemistries in the biosphere are intimately related.

Global cycle of sodium. Sodium is found among major elements that have been accumulated in the melted Earth's crust. The main mass of this element precipitates at the final stages of magmatic crystallization, and partially remains in post-magmatic solutions. Sodium is positioned midway between the stable alumosilicon-oxygen groups in the crystal chemical structure of silicates and is therefore amenable to an easy release from weatherworn hypogene silicates. The concentration of Na_2O in the "granitic" layer of Earth's crust is 2.71% and that in the sedimentary shell, 1.5%. Accordingly, the mass of sodium in the granitic layer is $116 \cdot 10^{15}$ tons, and in the sedimentary shell, $26.7 \cdot 10^{15}$ tons (see Table 5.1).

Sodium, on its release from the crustal crystalline matter, is transported as an easily soluble salt cation in the continental run-off into the ocean where its content amounts to $14.7 \cdot 10^{15}$ tons.

The main migratory flux of sodium in the biosphere is associated with its river streams from land transporting $0.185\,10^9$ ton/year of this element. Simultaneously, sodium is carried out as a component of stream loss suspension, mostly persisting in a sorbed state. Given the average sodium concentration in stream loss suspension 4.6 mg/liter, the total mass of this element transported as a suspension component amounts to $0.19 \cdot 10^9$ tons per year.

About $1.3 \cdot 10^9$ ton/year of water-soluble sodium is involved in the mass-exchange cycle between the ocean surface and troposphere, and about $0.14 \cdot 10^9$ ton/year between the land surface and troposphere. The oceanic air masses supply over $0.1 \cdot 10^9$ ton/year of water-soluble sodium to the land. Concurrently, about $0.01\,10^9$ ton/year of sodium in a sorbed state is carried over by the wind from the land surface to the ocean.

The predominance of the Na^+ cation in the biosphere explains the occurrence of large masses of sodium in all types of natural waters where it is bound in the equivalent proportions to anions Cl^-, SO_4^{2-}, and, partly, to $[HCO_3]^-$. In the pedosphere, sodium plays an important role in the cation-exchange processes. The high content of sodium in the absorbing soil complex facilitates the dispersion of soil aggregates and the formation of solonetzs. Sodium takes an active part in soil salinization where it binds with Cl^- and SO_4^{2-} to form salts. The sodium mass in the pedosphere has not as yet been quantified.

Table 5.1. Mass Distribution of Sodium and Chlorine in Biosphere

Major reservoirs	Sodium, $1 \cdot 10^9$ tons	Chlorine, $1 \cdot 10^9$ tons
Living matter:		
World's land	3.0	5.0
World's ocean	0.09	0.03
Pedosphere (organic remnants and humus)	0.3	0.3
Ocean (solubilized ions)	14740000	26500000
Earth's crust:		
sedimentary shell	26700000	6500000
granitic layer	166000000	1700000

Alongside its active involvement in the continental halogenesis, the enormous accumulation of sodium in the ocean allows us to characterize sodium as a typical thalassophilic element.

In the living organisms, sodium salts, mostly chlorides, play an important role. Sodium chloride is an indispensable component of animal fluid tissues (blood, blood plasma, lymph) and of the cell sap of plants where it is a major factor in maintaining the acid-base equilibrium, in controlling the osmotic pressure and water content in tissues and in performing a number of other important functions. By virtue of its important biological role, sodium chloride is assimilated in large amounts by vegetable and, especially, animal organisms; its deficiency causes severe dysfunctions.

Various authors disagree in the estimation of the average sodium concentration in living matter. According to Bowen (1966), the average sodium concentration in vegetable biomass of the World's land is about 0.12% (on a dry weight basis), which gives $3 \cdot 10^9$ tons of sodium for the terrestrial biomass. The Na concentration in the oceanic living matter is much higher reaching 3.3% (on a dry weight basis); however, in the oceanic biomass, the quantity of bound sodium is less by two orders of magnitude than in the terrestrial biomass.

The global biological turnover of sodium is strongly suggestive of the thalassophilicity of this element. On earth, the living matter utilizes annually about $4.6 \cdot 10^9$ tons of sodium; of this, the terrestrial biological turnover accounts for $0.2 \cdot 10^9$ tons, and the oceanic, for an amount greater nearly by a factor of 20.

Sodium salts are easily leached out of the plant remains, and for this reason, the sodium concentration in dead organic matter and in humus is rather small, about 0.01%, with its respective mass of $0.2\text{-}0.3 \cdot 10^9$ tons. Sodium is actively

taken up by sea sediments, which accounts for its high percentage in the sedimentary shell.

The global cycle of chlorine bears much resemblance to that of sodium. Chlorine is a typical thalassophilic element. Most chlorine, mainly in the form of soluble Cl^- ions, is accumulated in the waters of the World's ocean (see Table 5.1). The percentage of chlorine in the granitic crustal layer is 0.021%, which makes up to a mass of $1.7 \cdot 10^{15}$ tons. In the sedimentary shell its concentration is 10-fold higher, 0.27%, with the respective mass of $6.5 \cdot 10^{15}$ tons (Ronov *et al.* 1976).

Much similar to sodium, among the forms for occurrence of chlorine in biosphere, the readily soluble Cl^- ions are predominant. They define the main features of the global mass-exchange cycle of this element among which the exceptionally high ability for aqueous migration should be noted. Substantial masses of chlorine, as well as of chlorine, have for many millions of years been migrating from the World's land surface to the ocean. A second, still more remarkable feature of the global geochemical cycle of chlorine as compared to that of sodium is the active migration of chlorine in atmosphere as a component of aerosols and the return of its substantial mass to land. The annual supply of chlorine from ocean to atmosphere is $2.4 \cdot 10^9$ tons (with allowance made for dry precipitation), whereas the global return from atmosphere to ocean is $2.2 \cdot 10^9$ ton/year. The difference of $0.2 \cdot 10^9$ ton/year is air-transported to land. Thus, a substantial mass of Cl^- is involved in the land-ocean-land cycle, and

Table 5.2. Mass Transport of Sodium and Chlorine in Biosphere

Mass exchange process	Sodium, $1 \cdot 10^9$ ton/year	Chlorine, $1 \cdot 10^9$ ton/year
Biological cycle:		
on land	0.2	0.3
in ocean	2.8	1.1
Mass exchange between ocean and atmosphere:		
ocean-atmosphere	1.3	2.4
atmosphere-ocean	1.2	2.2
Mass exchange between land and ocean:		
overland run-off to ocean		
in solution	0.19	0.26
in suspension	0.19	nil
Atmospheric transport from ocean to land (ions)	0.1	0.2

for this reason, chlorine is referred to as a cyclic element in chemical meteorology (see Table 5.2).

In arid regions, especially those devoid of stream discharge, chlorine together with sodium and other halogenous elements become accumulated in the pedosphere and in closed reservoirs.

Chlorine is a physiologically important element, and it occurs in living organisms in the form of hydrochloric acid and its salts of which the most common is sodium chloride, as well as a constituent of various chlorinated organics. The average chlorine concentration in terrestrial living matter is 0.2% (dry weight), and in oceanic phytomass appreciably higher, about 1% (Bowen 1966). Reasonable estimates of chlorine content are $5.0 \cdot 10^9$ tons for terrestrial living matter and $0.17 \cdot 10^9$ tons for oceanic photosynthetic organisms. The chlorine concentration in the dead organic matter of pedosphere and humus is about 0.01%, or about $0.3 \cdot 10^9$ tons.

The biological turnover of chlorine on land is about $0.34 \cdot 10^9$ ton/year. In marine organisms, the chlorine content is high enough to amount to about 3% of dry biomass. During one year, the biota of the World's ocean involves in its biological cycle about $4.4 \cdot 10^9$ tons of chlorine, which is one-order of magnitude higher than that on land.

It follows from the above that the global mass-exchange cycles for sodium and chlorine share much in common, viz., predominance of easily-soluble forms, active aqueous migration from land to ocean, substantial atmospheric retransport from ocean to land, and a pivotal role of both elements in halogenesis. An essential feature of the biospheric geochemistry of these elements is their marked thalassophilicity which is manifest in the predominance of oceanic biological turnover over the terrestrial biological turnover (see Table 5.2). The physiological importance of the main compound of these two elements, sodium chloride, allows, in a sense, to raise them to a status of biogeochemical congeners.

Simultaneously, the distribution of chlorine and sodium masses in the biosphere is basically different. The enormous amounts of sodium, accumulated in sedimentary rocks and in ocean ($40 \cdot 10^{15}$ tons), account for a mere 19% of its mass contained in the original granitic crustal layer from which sodium was gradually removed to enter the mass-exchange cycle. For chlorine, the distribution pattern is quite distinct. In sedimentary rocks and in its main reservoir, the ocean, the chlorine content is almost 20 times its content in the granitic layer. If one imagines a hypothetical breakdown of the huge granitic layer, then the released mass of chlorine would be less than its mass currently found in the ocean. Apparently, the sources for supply of these elements to mass-exchange cycles in the biosphere were different. Sodium was supplied owing to the hypergene mobilization (weathering) from the granitic layer of continental crust, and chlorine, owing to the outgassing of the mantle and to the eruption of volcanic gases. Accordingly, it appears expedient to discuss

separately the global cycles for elements supplied to the biosphere from the two mentioned sources.

5.2. Cycles and Mass Distribution for Elements Supplied to the Biosphere Through Outgassing. Global Carbon Cycle

Cyclic processes of carbon mass exchange are of particular importance for the biosphere.

The mass distribution for this element is as follows. According to the updated data (Voitkevich 1986), there is $2450 \cdot 10^9$ tons of carbon dioxide in the atmosphere, or $668 \cdot 10^9$ tons of carbon. In the ocean, carbon, along with its occurrence in living organisms, is present in two major forms: as a constituent of organic matter (in solution and partly in suspension) and as a constituent of interconvertible inorganic ions HCO_3^-, CO_2^{2-}, and CO_2.

The average concentration of soluble organic matter in the ocean has been estimated to be 1.5 mg/liter (based on organic carbon, C_o), and that of disperse suspended organic matter, about 0.02 mg/liter C_o (Lisitsin *et al.* 1983). The overall content of carbon in the total volume of World's ocean is then about $2100 \cdot 10^9$ tons C_o. Along with the organic carbon, there is in the ocean also a mineral carbon that makes part of the carbonate system, C_c, mainly as a constituent of hydrocarbonate ion HCO_3^-. The average HCO_3^- concentration in ocean is 143 mg/liter, the overall hydrocarbonate mass being $196000 \cdot 10^9$ tons. Of this, the C_c accounts for $38600 \cdot 10^9$ tons.

As has been pointed out earlier, the bulk of living organisms are confined to land, and their mass, converted to a dry weight, amounts to $2500 \cdot 10^9$ tons. However, this quantitative characteristic refers to the World's land vegetation unperturbed by human activities. There are good reasons to believe that human intervention has reduced the mass of natural terrestrial vegetation by 25%, which gives an estimate of $1880 \cdot 10^9$ tons for today's vegetation. The average carbon concentration in the dry matter of terrestrial vegetation is 46% (see Table 1.2) and, consequently, the carbon mass in the land vegetation unaffected by human activity might be $1150 \cdot 10^9$ tons, as compared to its current estimate of about $863 \cdot 10^9$ tons.

According to the recent data by Romankevich (1988), the oceanic biomass of photosynthetic organisms contains $1.7 \cdot 10^9$ tons C_o. This is greater by an order of magnitude over the earlier estimate of $0.1 \cdot 10^9$ tons (Dobrodeyev *et al.* 1976). Besides, the ocean harbors a large number of consumer organisms, with $2.3 \cdot 10^9$

Table 5.3. Mass Distribution of Carbon in the Earth's Crust (according to the data by Ronov and Yaroshevsky (1976), with author's supplements)

Part of Earth's crust, mass of, $1 \cdot 10^{18}$ tons	Average concentration, %			Mass, $1 \cdot 10^{15}$ tons				C_c/C_o
	CO_2	C_c	C_o	CO_2	C_c	C_o	$C_c + C_o$	
Earth's crust, the total of, (28.46)	1.44	0.38	0.07	409	108	20	128	5.4
Earth's crust, types of: continental (18.07)	1.48	0.40	0.08	267	72	14	86	5.1
subcontinental (4.30)	1.37	0.36	0.07	58	16	3	19	5.3
oceanic (6.09)	1.35	0.36	0.05	82	21	3	24	7.0
Continental crust: sedimentary layer (1.85)*	9.57	2.61	0.50	177	48	9	57	5.3
"granitic" layer (6.83)	0.81	0.22	0.05	55	15	3	18	5.0
"basaltic" layer (9.39)	0.37	0.10	0.02	35	9.4	1.9	11	5.0
"Granitic" layer, the total of, (8.24)	0.81	0.22	0.05	67	18	4	22	4.5
Earth's sedimentary shell** (2.4)	12.38	3.37	0.62	297	81	15	96	5.4
Phanerozoic sedimentary deposits (1.3)	14.96	4.08	0.56	194	53	7	60	7.5

C_c, carbonate carbon; C_o, carbon of organic matter; *, effusive rocks included; **, effusive rocks excluded

tons C_o in their mass. *In toto*, carbon as contained in the living oceanic organisms makes up to fractions of a percent with respect to carbon found in the vegetational mass of World's land.

In the terrestrial pedosphere, there is a substantial amount of dead organic matter such as incompletely decayed plant remains forming forest litter and peat accumulations, as well as humus. The mass of litter is close to $200 \cdot 10^9$ tons, and that of peat, $500 \cdot 10$ tons. The quantity of humus in the pedosphere has been estimated to be $2400 \cdot 10^9$ tons (Kononova 1974). The total of carbon confined to the dead organic matter of World's land is $1500\text{-}1600 \cdot 10^9$ tons.

To briefly summarize, one may say that the least amount of carbon is found in the atmosphere, somewhat more, in the living matter of land, and still more, in the dead organic matter of pedosphere. A substantial mass of carbon in the form of hydrocarbonates is contained in the ocean, 10 times higher than the total of carbon in living matter, atmosphere, and pedosphere.

The above data are tentative and, in a sense, reflective of the current level of our knowledge. The carbon mass distribution in the biosphere as obtained by other authors using other approaches, (Vinogradov 1967; Ivanov *et al.* 1988; Romankevich 1988; Bolin 1979) although somewhat different, are not basically at variance with our results.

The mass distribution of carbon in the Earth's crust is essential for an understanding of the global biochemistry of this element. One may form a general idea of the crustal carbon distribution in examining Table 5.3. As is seen, carbonate carbon is the major form for the occurrence of carbon in the Earth's crust. The carbonate-to-organic carbon mass ratio, C_c/C_o, is about 5 for the Earth's crust as a whole as well as for its main layers (sedimentary, granitic, and basaltic) and crustal types: continental, subcontinental and, less rigorously, oceanic, for which this ratio is somewhat higher.

The sedimentary layer of the Earth's crust (stratisphere) serves as a major reservoir for carbon. The concentration of C_c and C_o in the sedimentary shell is by an order of magnitude higher than that in the granitic and basaltic layers of lithosphere. Despite the fact that the volume of the sedimentary shell is merely one tenth the crustal volume, the sedimentary layer accounts for 75% of C_c and 75% of C_o. Most of C_o mass is represented by dispersed organic matter. Localized accumulations of C_o in the form of oil and coal deposits are of secondary importance.

According to the available evidence, the oil fields account for $0.2 \cdot 10^{12}$ tons of carbon, and the coal deposits, for $6 \cdot 10^{12}$ tons. To summarize, this is three orders of magnitude less than the carbon mass of dispersed organic matter contained in the sedimentary shell. The general carbon distribution in the biosphere is as listed below:

Reservoirs:	Mass, $1 \cdot 10^9$ tons C
Atmosphere, CO_2	668
World's land:	
vegetable biomass prior to human activities	1150
natural vegetable biomass of to-day	900
Pedosphere	
forest litter	100
peat	250
humus	1200
pedosphere, total	1550
Ocean:	
photosynthetic organisms, biomass	1.7
consumer organisms, biomass	2.3
organic matter, in solution and suspension	2100
hydrocarbonate ions in solution	38539
Earth's crust:	
sedimentary shell, C_o	15000000
sedimentary shell, C_c	81000000
continental granitic layer, C_o	4000000
continental granitic layer, C	18000000

Thus, there are two major forms for the occurrence of carbon in the Earth's crust: carbonate and organic compounds. It should be emphasized that both are biogenous. Carbonates of non-biogenous origin, for example, volcanic carbonatites, are a fairly rare exception to the rule. A connecting link between the carbonate and organic species is CO_2 which serves as an essential starting material for both the photosynthesis of organic matter and the microbial formation of carbonates.

The biotic activity of organisms is accompanied by a fractionation of the isotopic composition of CO_2 carbon. This effect was predicted by Vernadsky (1926) long before the first experimental evidence became available. Carbon of terrestrial occurrence consists of two stable isotopes ^{12}C and ^{13}C supplemented with ^{14}C which is a radioactive species with a half-life of 5730 years and is present in vanishingly small amounts.

The $^{12}C/^{13}C$ ratio varies in natural objects within a range of 88-94. In living matter, this ratio is about 90.5, in carbon dioxide of atmosphere and hydrosphere, 89.5, and in carbonate deposits, about 88.6. The relative increment, $\delta^{13}C$,

$$\delta^{13}C = \left[\frac{^{13}C/^{12}C(\text{sample})}{^{13}C/^{12}C(\text{reference})} - 1 \right] \cdot 1000\%$$

The PDB standard, a calcium carbonate carbon from *Belemnitella Americana* of the Late Cretaceous, PD formation, with a value of $^{13}C/^{12}C = 1123{\cdot}72{\cdot}10^{-5}$, has been chosen for a reference. The value of $\delta^{13}C$ with a "+" sign corresponds to a relative increase in ^{13}C isotope content, and with a "–" sign, to its decrease in a sample studied with respect to the reference.

By the action of the enzyme ribulose bisphosphate carboxylase, a major link in photosynthesis, the ^{12}C isotope is taken up at a higher rate; owing to this, the organic matter becomes enriched with this isotope. Microbiological processes stimulate this uptake. For this reason, the methane of microbiological origin has a maximum content of the light isotope. Since the photosynthetic organic matter is built on ^{12}C, carbonates they are to a larger extent rich in the heavy ^{13}C isotope.

According to Schidlowski (1980), one may, in a broader sense, accept that the CO_2 carbon as evolved from the mantle on degassing has $\delta^{13}C = -5‰$, the carbon of organic matter has $\delta^{13}C = 0 \pm 2.5‰$ and the carbon of sedimentary carbonates has $\delta^{13}C = -25 \pm 5‰$. Schidlowski has shown by his calculations that the carbon isotope ratio in sedimentary shell corresponds to the C_c/C_o mass ratio. Thus, the study of carbon isotope ratio for sedimentary rocks of different age has provided evidence, first, that the CO_2 assimilation in photosynthesis took the same course during a period of at least 3.5 billion years. Consequently, this process, universal for all the producers involving ribulose bisphosphate carboxylase, was reproducible by all generations of photosynthetic organisms from their very onset. Second, the results for $^{13}C/^{12}C$ isotope composition and C_c/C_o mass distribution have been found to be in good agreement. Within a very extended period of time, the initial CO_2 was subject to a regular partition between photosynthesis and carbonate formation. In this process, over 80% of carbon supplied to the atmosphere by mantle outgassing became bound as carbonates.

The carbonate formation and photosynthesis should be viewed as two general processes in the global activity of living matter extending over a period of 3-3.5 billion years. The C_c-to-C_o mass ratio is quite an important index specifying the "growth limit" for living matter at sequential stages of geological history. The C_c-to-C_o mass ratio tended to decrease regularly within the last 1.6 billion years. According to the data by Ronov (1976), in the sedimentary layer of the Upper Proterozoic (1600-570 million years), the C_c/C_o ratio was 18; that of the Paleozoic (570-400 million years), 11; of the Mesozoic (235-66 million years), 5.2, and of the Cainozoic, 2.9. The never-interrupted increase in the relative content of organic matter in the ancient stream loss provides evidence for a progressive productivity of terrestrial photosynthetic organisms and for the ever-growing importance of the World's land vegetation in global fixation of CO_2. Both the carbonate formation and the photosynthesis of organic matter share in the common tendency for removal from the atmosphere of

carbon dioxide continually supplied from the mantle. Possibly, these processes make part of a global mechanism for maintaining a low concentration of CO_2 in the Earth's gas shell, which is an essential factor in the so-called "greenhouse effect".

Now, let us turn our attention to the natural processes of carbon mass-exchange dynamics in the biosphere. Today's global biogeochemical carbon cycle encompasses two large cycles of lower rank. The first of these bears relevance to the photosynthetic binding of carbon dioxide into organic matter and to the novel formation of CO_2 via transformation of the primary organic matter by heterotrophs and edaphic microorganisms. If this cycle is completely closed, then the whole of photosynthetically absorbed carbon dioxide would have returned to its initial reservoir, the atmosphere. In reality, this is not the fact.

The productivity of the World's land vegetation not interfered with by man was $172.5 \cdot 10^9$ tons of dry organic matter containing 46% of carbon, that is, about $80 \cdot 10^9$ tons. At the present time, the mass of natural vegetation has presumably reduced to about $60 \cdot 10^9$ tons of C. The estimated productivity of oceanic photosynthesis has been 40 (Bolin 1979) to $50\text{-}60 \cdot 10^9$ ton/year C_o (Romankevich 1988). Thus, the initial planetary productivity of living matter of $130\text{-}140 \cdot 10^9$ ton/year C_o has, in all probability, reduced to $110\text{-}120 \cdot 10^9$ ton/year C_o.

The amount of the annually decaying organic matter has as yet evaded an exact determination. Nonetheless, there are good reasons to believe that a substantial amount of organic carbon is continually removed from the cycle in question. On land only, the humic accumulation of carbon in the pedosphere within a period of no longer than 1000 years has been twice as much as its content in the atmosphere. One may presume therefore that the stable long-lived humic compounds acquire some 30% of carbon annually from the died-off organs of plants, and the complete renewal of humus in soils extends over an average period of $1\text{-}1.5 \cdot 10^3$ years. It stands to reason that the period of complete renewal is susceptible to variations depending on the hydrothermal conditions.

The synthesis and degradation of organic matter in the ocean are essentially distinct from these processes on land. The phytoplankton provides for a larger part of photosynthetic organic matter. Its dry mass is at least three orders of magnitude smaller than the vegetable mass of the World's land, whereas the annual production by the two is close in value. This should be attributed to the much faster life cycles of plankton organisms, the major photosynthetic producers in the ocean, in comparison with the terrestrial plants.

In relating the biomass of terrestrial vegetation ($2500 \cdot 10^9$ tons) to its annual production ($172.5 \cdot 10^9$ tons of dry organic matter), one will infer that the vegetable mass of the World's land takes a period of about 15 years for its

complete renewal. In the ocean, the situation appears to be quite different. One may presume, with allowance for a 10-fold discrepancy in the estimates of phytoplankton mass and productivity by various authors, that the phytoplankton mass cycle takes 1-2 days to complete, whereas the renewal of the total of oceanic biomass requires about a month. The annual production by photosynthesis in ocean varies, according to a number of estimations, from 20-30 to $100 \cdot 10^9$ tons C_o, the average being $50\text{-}60 \cdot 10^3$ tons. By virtue of the fact that the plankton-synthesized organic matter is almost completely assimilated by the subsequent trophic cycles, the precipitated remains are not in excess of $0.1 \cdot 10^9$ ton/year. Thus, the annual uptake of living matter on land and in ocean is about $440 \cdot 10^9$ tons CO_2 ($120 \cdot 10^9$ tons C_o), most of which is recycled into the ocean and atmosphere.

The second large biogeochemical carbon cycle involves the interaction between atmospheric CO_2 and natural waters. The gases of troposphere and the surface layer of ocean persist in a state of kinetic equilibrium.

The solubility of gases in water is dependent on pressure, temperature, and the occurrence of soluble salts. The gas solubility increases with partial pressure according to the Dalton-Henri law. In fresh water, the gas solubility is higher over that in saline water; still, the quantity of fresh water on the Earth's surface is incomparably less than that of saline water. For that reason, the fresh waters contribute but modestly to the overall CO_2 balance. The CO_2 solubility decreases with temperature in the following manner (milliliters of CO_2 per liter of water): 0°C, 1.71; 10°C, 1.19; 20°C, 0.88; 25°C, 0.76. The mean concentration of carbon dioxide dissolved in sea water has been accepted as 0.75 ml/liter (Lisitsin 1983). However, CO2, as distinct from other gases, enters into a chemical reaction with water to yield carbonic acid: $CO_2 + H_2O \rightleftarrows H_2CO_3$. This acid is a dibasic one and dissociates stepwise to produce a carbonate-hydrocarbonate system:

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$$

All the system components having been accounted for, one may accept that 1 liter of oceanic water contains about 50 cm^3 of dissolved CO_2.

The chemical interaction of CO_2 and H_2O has provided for the occurrence of enormous amounts of carbonic acid in the World's ocean. The mass of hydrocarbonate ions in the World's ocean is $196 \cdot 10^{12}$ tons, which, converted to CO_2, amounts to $141 \cdot 10^{12}$ tons. This mass is a nearly 60-fold excess over the mass of carbon dioxide found in the atmosphere. One will easily perceive therefore that the ocean is a major reservoir for CO_2 on the Earth's surface. The CO_2 mass exchange between atmosphere and ocean is effected through

the uptake of carbon dioxide into the carbonate-hydrocarbonate system followed, under appropriate conditions, by the release of CO_2 from the ocean surface. In a broad outline, the movement of CO_2 masses may be visualized in the following manner. Carbon dioxide becomes actively dissolved in the cool waters of subpolar ocean regions. Since the water density is known to increase on cooling, the masses of cooled oceanic water go down to depth and, merged into powerful cold streams, start moving toward the equator. *En route*, they gradually warm up, diminish their density, rise surfaceward and become relieved of excess CO_2. After the imaginative remark of Vinogradov (1967) the ocean operates as a colossal pump taking in CO_2 from the atmosphere in subpolar regions and releasing it in tropical regions. The CO_2 mass exchange between the surface ocean layer and troposphere is influenced, to a sizeable extent, by the living matter of plankton, light energy, and seasonal thermal conditions.

Based on his measurements of the rate of concentrational decrease of the radioactive ^{14}C isotope after large-scale atmospheric nuclear tests in 1963, Bolin (1979) arrived at a conclusion that roughly $100 \cdot 10^9$ tons of CO_2 per year (or about $30 \cdot 10^9$ tons of C) is involved in the CO_2 uptake-release cycle at the surface of the World's ocean.

The entrainment of hydrocarbonates by the wind as water dust from the perturbed ocean surface and their precipitation into the ocean also contribute to a certain extent to the carbon mass exchange between atmosphere and ocean. The HCO_3^- concentration in the atmospheric precipitation over the ocean is 0.33 mg/liter (Bezborodov *et al.* 1984). The annual precipitation of HCO_3^- is $0.136 \cdot 10^9$ tons; of this, C_c accounts for $0.027 \cdot 10^9$ tons. The annual transport to land of air-borne HCO_3^- of oceanic origin is $0.015 \cdot 10^9$ tons, which corresponds to $0.003 \cdot 10^9$ tons of carbon.

The average concentration of HCO_3^-, precipitated over the World's land, is about 10 mg/liter. $6.9 \cdot 10^9$ tons of HCO_3^-, or $0.14 \cdot 10^9$ tons of C are involved in the water cycle over the land. The contribution due to the air-borne transport of hydrocarbonates from ocean is of minor importance.

The estimation of C_c and C_o masses annually eliminated from the biogeochemical cycles in ocean is an arduous task. The carbonate-hydrocarbonate system includes, in its entirety, the precipitation of calcium carbonate as a deposit:

Atmosphere CO_2

$\uparrow\downarrow$

Ocean $H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^- \rightleftarrows H^+ + CO_3^{2-} + Ca^{2+}$

$\uparrow\downarrow$

Deep-sea deposits $CaCO_3$

The binding of carbon into carbonates is related to the activity of living organisms but is effected through a biochemical mechanism quite distinct from that by which carbon is incorporated into organic matter. The formation of carbonate deposits is to a significant extent determined by the run-off supply of Ca^{2+} ions. The Ca^{2+} ion stream loss is roughly $0.53 \cdot 10^9$ ton/year, which can provide for a $CaCO_3$ precipitation rate of $1.33 \cdot 10^9$ ton/year. Otherwise stated, this corresponds to a loss of $0.57 \cdot 10^9$ tons CO_2, or $0.16 \cdot 10^9$ tons C from the carbonate-hydrocarbonate system.

With reference to the discussed above carbonate-to-organic carbon mass ratio, the carbonate deposition 1.5 billion years back was markedly predominant over the burial of organic matter ($C_c/C_o = 18$). With time, the C_o started to gradually increase. In the Cainozoic deep-sea deposits, the C_c/C_o ratio dropped to 2.5, or even to 1.4. This ratio having been maintained at the present time, the annual supply of organic carbon to the World's ocean pelagic deposits must be 0.06-$0.11 \cdot 10^9$ tons, which makes an average of $0.08 \cdot 10^9$ tons. With reference to the data by Ronov (1976), in the Neogene, the rate at which carbon was lost into sea deposits varied as 0.020 to $0.085 \cdot 10^9$ ton/year for C_c and 0.014 to $0.020 \cdot 10^9$ ton/year for C_o. These values compare well with the above estimate.

The World's land run-off plays an important role in the global carbon mass exchange. The continental run-off supply of HCO_3^- is $2.4 \cdot 10^9$ ton/year, that is, $0.47 \cdot 10^9$ ton/year for carbon. Besides, the stream water contains organic matter dissolved in it at carbon concentration of 6.9 mg/liter (Livingston 1963), which makes up to an annual loss of $0.28 \cdot 10^9$ ton/year. The average carbon concentration of suspended insoluble organic matter in the stream run-off is 5 mg/liter, which gives a loss of about $0.2 \cdot 10^9$ ton/year. Most of this mass fails to reach the open ocean and becomes deposited in the shelf and the estuarine delta of rivers. One may presume therefore that $0.5 \cdot 10^9$ tons of C_c and about the same amount of C_o is annually lost from the World's land surface.

The formation of carbonates as well as the accumulation of organic matter are not confined solely to ocean; these processes occur also on land. The mass of carbonates annually produced in the soils of arid landscapes appears to be high enough but, as yet, it evades even a tentative quantification.

Thus, the global dynamics of carbon mass transport in the biosphere is determined by two large cycles. The first of these is provided for by the assimilation of CO_2 and decomposition of H_2O through photosynthesis of organic matter followed by its degradation to yield CO_2. The second cycle involves the uptake-release of carbon dioxide by natural waters via chemical reaction of CO_2 and H_2O leading to the buildup of a carbonate-hydrocarbonate system. The two cycles are intimately related to the activity of living matter. The living matter of biosphere, the global water cycle, and the carbonate-hydrocarbonate system regulate the cyclic mass exchange of carbon between atmosphere, land,

Table 5.4. Mass Transport of Carbon in Biosphere

Mass exchange process	Mass of carbon, $1 \cdot 10^9$ tons per year
World's land	
Biological cycle (photosynthesis-degradation of organic matter)	85
HCO_3^- ion mass exchange between land and troposphere	
supply to troposphere	0.136
rainfall washout from troposphere	0.139
Stream loss of:	
solubilized inorganic ions	0.47
soluble organic matter	0.28
suspended organic matter	0.20
Transport of air-borne HCO_3^- ions of oceanic origin to land	0.003
World's ocean	
Turnover of planktonic photosynthetic organisms	50
CO_2 uptake by ocean	30
CO_2 release by ocean	30
C_o, deposited in precipitation	0.08
C_c, deposited in precipitation	0.16

and ocean. The migration of carbon masses in the global cycle is summarized in Table 5.4.

A specific feature of the two major cycles is their openness manifest in the removal of some carbon in the form of dead organic matter and carbonates.

The continual removal of carbon from the global cycle and its burial in the sea deposits is of cardinal importance for the development of biosphere. Ronov and Yaroshevsky (1976) have made thorough calculations and shown that the carbon contents in the granitic crustal layer amount to $4.1 \cdot 10^{15}$ tons (organics) and $18 \cdot 10^{15}$ tons (carbonates), the total being $22.1 \cdot 10^{15}$ tons. This quantity is about 4 times less than that in the sedimentary shell. It should be inferred therefore that carbon could not be supplied to the biosphere via hypergene transformation of the rocks in the granitic layer of lithosphere. The atmosphere has served as a reservoir for supply of carbon for nearly two billion years. Still, the atmospheric content of this element in the form of carbon dioxide is rather limited. The never-interrupted elimination of carbon from the atmosphere might have led to a depletion of CO_2 and to a gradual reduction

of living matter, with the eventual extinction of life on our planet. Fortunately, this has never happened owing to the continuous supply of carbon dioxide from the planet surface, and the concentration of this gas in the atmosphere is maintained at a constant level. The only natural source of additional supply of CO_2 are volcanic gases.

Ronov (1976) has made an estimation of the volume of all types of sedimentary rocks arisen in the Phanerozoic and calculated the amount of carbon contained in carbonate rocks and dispersed organic matter. He has also determined the volume of the laval effluents for the period when the carbonate deposits were being formed. As shown by his findings, the carbonate-bound masses of CO_2 and the organic carbon dispersed in the ancient rocks varied with the fluctuations of volcanic rock masses. In the epochs of vigorous volcanic eruptions and efflux of enormous masses of lava, the deposition of both carbonate rocks and dispersed organic matter proceeded at a notably high rate (see Fig. 14). Presumably, the laval volume may serve to indicate the extent of erupted volcanic gases. Over a period of 570 million years, $71300 \cdot 10^{12}$ tons of carbonate-bound carbon and $8100 \cdot 10^{12}$ tons of dispersed organic carbon became buried in sedimentary rocks. The available evidence is suggestive, on the one hand, that the emergence and development of life were linked, rather unexpectedly, to the mantle degassing and to the supply of carbon dioxide from the Earth's interior. On the other hand, the evolvement and functional maintenance of the biosphere were determined by the geochemical activity of living matter. If the living organisms had failed to provide for the geochemical carbon cycle maintaining low concentration of CO_2 in the atmosphere, then the buried mass of bound carbon (about $1 \cdot 10^{17}$ tons) would have evolved as $4 \cdot 10^{17}$ tons of atmospheric carbon dioxide, that is, thousands of times higher over its actual level. One will easily have perceived the ensuing catastrophic impact therefrom on life because of the greenhouse effect.

The atmospheric CO_2 molecules are known to absorb the infrared (thermal) radiation of the Earth and to emit light energy toward the Earth's surface. Sharply increased carbon dioxide level in the atmosphere as hypothetically mentioned above might have caused a very high rise in temperature and a warming of the planet surface to a complete evaporation of the World's ocean.

The increased influx of carbon dioxide at the periods of active volcanism was attended, in all probability, by an overall climatic warming-up and a reduced temperature contrast between high and low latitudes. Possibly, the widespread of red products of weathering typical of tropic landscapes in the Neogene and their complete disappearance from extratropical territories in the Pleistocene might be associated with the reduced supply of volcanic CO_2 at the end of alpine tectogenesis.

Some researchers (Dobrodeyev *et al.* 1976) believe that the alternation of glacial and interglacial periods in the Pleistocene was mainly due to fluctuations

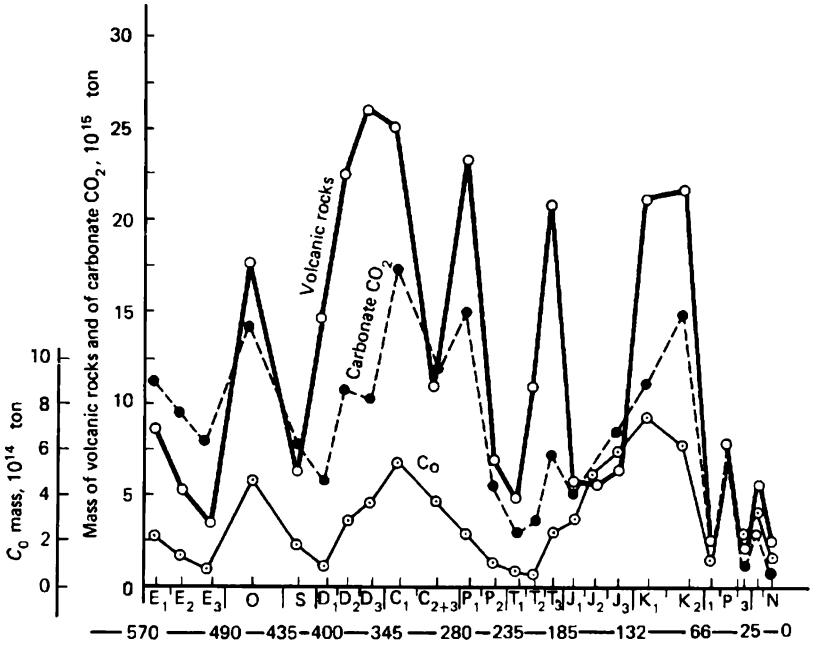

Mass of volcanic rocks and of carbonate CO_2, 10^{15} ton
C_0 mass, 10^{14} ton
Volcanic rocks
Carbonate CO_2
C_0
E1 E2 E3 O S D1 D2 D3 C1 C2+3 P1 P2 T1 T2 T3 J1 J2 J3 K1 K2 P3 N
570 490 435 400 345 280 235 185 132 66 25 0

Fig. 14. Temporal variations of volcanic rock mass, total carbonate CO_2 mass, and organic carbon mass (C_0) buried in the sedimentary continental layers (after Ronov 1976)

of carbon dioxide in the atmosphere. It may also be hypothesized that the spread of land ice and the drastic reduction of forest areas with their typically high biomass were favorable to an elevated CO_2 level in the atmosphere and to climatic warming-up. In turn, the resulting contraction of glaciated areas and the regain by forests of their former territories was attended by an increased CO_2 uptake from the atmosphere and by binding CO_2 to the biomass and organic matter of the pedosphere. The resultant effect was a gradual cooling and the onset of a new glaciation followed by the reduction of forest areas and the repetition of the whole cycle. It is to be emphasized that all those alterations in the carbon cycle could proceed in a natural way unperturbed by productive activities of man.

The global carbon cycle is affected in a definite manner by human productive activities. The ever-increasing expansion of plowland areas, building of new cities and highways, forest cutting, etc. have made the terrestrial biomass decrease by about 25%. Accordingly, the proportions (both quantitative and qualitative) of chemical elements involved in the biological cycles, and the

masses of uptaken carbon and released oxygen also changed. A still greater destructive effect is caused by the combustion of fossil fuels attended by the consumption of appreciable masses of oxygen from the atmosphere and by the production of gaseous carbon compounds. Of these, predominant are CO and CO_2. The overall supply of carbon from technogenic sources to the atmosphere has been estimated as $5 \cdot 10^9$ tons per year. This amount as involved in the global carbon cycle leaves the distribution of this element in the biosphere practically unaffected but potentially may be a factor in the greenhouse effect.

To conclude, it should be noted that the consumption of over 90% of combustibles is confined to the Northern Hemisphere, which leads to an uneven distribution of carbon oxide. Maximum CO concentrations have been recorded within a strip between 40° and 50° N, where the major industrial centers are situated.

5.2.1. Effect of Living Matter on Geochemistry of Oxygen and Hydrogen in Biosphere

The main mass of oxygen on land is found in the Earth's crust as a constituent of crystalline silicate matter. Oxygen also accounts for a larger part (86%) of the hydrosphere. For the biosphere, however, free molecular oxygen occurring both in the atmosphere and hydrosphere is of exceptional importance. Oxygen, evoked to existence by biotic processes, is a major factor in the persistence of main forms of life and is determinative of the most essential reactions in the biosphere.

The living matter has carbon, oxygen, and hydrogen for its main constituents. The distribution and dynamics of these elements in the biosphere are irrevocably interwoven, of which the researchers of the subject became aware at the very earliest stage. It is noteworthy, that the production of free oxygen is linked to the utilization of solar energy and, therefore, can be effected only on the Earth's surface either via the abiogenous route by photolysis of water vapors, or via biological photosynthesis.

The initial material for the production of oxygen by photolysis and photosynthesis is water. The binding of 1 g of carbon to produce an organic substance by photosynthesis is accompanied by the release of about 2.7 grams of oxygen eliminated from the split water molecules. As has earlier been mentioned, the occurrence of organic matter has been recorded in ancient sedimentary deposits going back for 3.8 billion years. Therefore, the production of oxygen by photosynthesis is a process operative within a very long period of time. The estimates by Ronov and Yaroshevsky (1976) show that the sedimentary Earth's shell contains about $15 \cdot 10^{15}$ tons of C_o (see Table 5.3). This is equivalent to $40 \cdot 10^{15}$ tons of O_2. The atmosphere of to-day contains

$1.185 \cdot 10^{15}$ tons of oxygen. Consequently, over $38 \cdot 10^{15}$ tons of oxygen has been consumed in oxidation processes.

Starting from the productivity of the World's land vegetation when intact by man, the annual release of oxygen can be estimated as $220 \cdot 10^9$ tons. At the present time, because of deforestation and factual extermination of natural vegetation over large territories, the vegetative productivity has dropped by some 25%, and the oxygen release has lowered to about $165 \cdot 10^9$ ton/year. The photosynthesis in the ocean, taking into account the C_o productivity of 40 to $60 \cdot 10^9$ ton/year, supplies annually to the atmosphere 110 to $160 \cdot 10^9$ tons of O_2, on average $130 \cdot 10^9$ tons.

The overall release of oxygen by the photosynthetic organisms of land and ocean amounts to about $300\text{-}350 \cdot 10^9$ tons per year. These values are close to those calculated by Walker (1980) featuring the following processes for the global oxygen cycle: release of oxygen by the World's land vegetation, $150 \cdot 10^{15}$ ton/year; release of oxygen by photosynthetic organisms of the ocean, $120 \cdot 10^{15}$ ton/year; aerobic respiratory absorption of oxygen, $210 \cdot 10^{15}$ ton/year; biological nitrification and other processes, $70 \cdot 10^{15}$ ton/year.

The amount of oxygen in the atmosphere is $1.185 \cdot 10^{15}$ tons. At a rate of oxygen release $280\text{-}300 \cdot 10^9$ ton/year, the said amount will take some 4000 years to reach its double. However, this may be envisaged only in theory, since the amount of organic matter decomposed during one year in a variety of ways is nearly equal to its annual production by photosynthesis, at a nearly null balance of oxygen uptake-release. Nonetheless, owing to a partial preservation of organic matter, free oxygen tends to accumulate gradually in the atmosphere.

The second migration cycle of free oxygen is associated with the mass exchange in the "troposphere-natural waters" system. One liter of water is capable of dissolving 2 to 8 cm^3 of oxygen. Therefore, the oceanic waters are a reservoir for 3 to $10 \cdot 10^9$ m^3 of dissolved oxygen. The cool water of high latitudes absorbs oxygen and, arrived in oceanic streams at the tropical belt, releases it. The uptake and release of oxygen occurs also during the annual alternation of cold and warm seasons. According to the estimates of Vinogradov (1967), about 0.5% of atmospheric oxygen, that is, $5900 \cdot 10^9$ tons, is involved in the annual mass exchange between atmosphere and ocean. This is almost a 20-fold excess over the biogenous production of oxygen.

Hydrogen and helium are two chemical elements which, owing to their negligibly small nuclear masses are capable of dissipation, that is, can escape the effect of the gravitational field of the Earth. On their transit to outer space, hydrogen and helium pass across the biosphere. Helium, being an inert species, forms no chemical compounds, whereas hydrogen, responsive to the biotic activity of organisms, enters into chemical reactions and is thus retained in the biosphere.

Hydrogen, both in the free (molecular) form and as a constituent of chemical compounds, is actively outgassed from the mantle. Substantial masses of H_2 are delivered to the Earth's surface via volcanic eruptions and post-volcanic processes and are also supplied in the course of biotic activity of hydrogen-releasing bacteria involved in the transformation of organic matter under anaerobic conditions; hydrogen is also produced by decomposition of water in electrochemical reactions and by the action of decay products from radioactive elements. Given the dissipation rate of hydrogen at $25 \cdot 10^3$ ton/year, its atmospheric content is a mere $0.18 \cdot 10^9$ tons. The overall loss of hydrogen over the entire period of Earth's existence has been estimated as $0.1 \cdot 10^{15}$ tons (Zavarzin 1984).

The accumulation of oxygen in the atmosphere stands in a close relation to the removal from it of hydrogen. At the early stages of Earth's history, the dissipation played a leading role in the removal of hydrogen produced by photolysis of water vapors. In this further course, the elimination of hydrogen through binding it into organic matter started to gain an ever-increasing importance.

In photosynthesis, 3 grams of water becomes split per 1 gram of bound carbon, the process releasing 0.34 gram of hydrogen for its incorporation into organic matter. $3500 \cdot 10^9$ tons of water was split and $390 \cdot 10^9$ tons of hydrogen was bound to produce the entire mass of intact vegetation of the World's land. At present, the annual supply of about $40 \cdot 10^9$ tons of hydrogen for the buildup of organic matter requires the cleavage of about $350 \cdot 10^9$ tons of water during the photosynthesis of natural vegetation on land and in the ocean.

As has been exemplified by carbon, the repeated cyclic processes of chemical element migrations facilitate the isotope differentiation. One of the most potent cyclic processes operative on the Earth's surface since the emergence of both atmosphere and ocean is the water cycle. It stands to reason that precisely the water mass-exchange cycle has become the most essential factor in the separation of hydrogen and oxygen isotopes.

Hydrogen is represented by two stable isotopes: protium, ^1H, and deuterium, ^2H (D). The abundance of ^1H is 99.984%, and that of deuterium, about 0.0156%. Oxygen is made up of three stable isotopes of abundance 99.759% for ^{16}O, 0.0374% for ^{17}O, and 0.203% for ^{18}O. The hydrogen and oxygen isotope composition of natural waters is expressed in terms of the δ relative increment, by analogy with the above formula for $\delta^{13}C$. The average isotope composition of oceanic water for which the values of δD and $\delta^{18}O$ are zero is used as an international standard.

The water cycle in the biosphere is concomitant with a directional fractionation of oxygen and hydrogen isotopes: the deuterium increase is in parallel to the heavy oxygen isotope ^{18}O increase according to a linear relationship $\delta D = 8\delta^{18}O + 10$ (Craig 1954). In evaporation, the water vapors become enriched

in light isotopes. For this reason, the values of δD and $\delta^{18}O$ for precipitated, surface, and ground waters are negative in sign. The extent of oxygen isotope separation increases with decreasing temperature. The overall effect of all these factors is that the most light water is contained in the arctic and antarctic land ice. The oceanic waters are characterized by a stable hydrogen and oxygen isotope composition. In thermal waters, the value of δD is little varied, whereas that of $\delta^{18}O$ tends to increase.

Currently, no evidence is available suggestive of a direct involvement of living organisms in the isotope fractionation of hydrogen and oxygen. At the same time, biogenous formations reflect the isotope composition of their habitat. This circumstance may be profitably used in paleogeographic and paleobiogeochemical reconstructions. For example, attempts have been made to reconstruct the temperature of ancient seas using the oxygen isotope composition of the carbonate skeleta of fossil molusks.

The organisms, while being directly engaged in the fixation of hydrogen in the biosphere through binding it into organic matter, are also assistant in the retention of hydrogen by the mineral matter of the pedosphere. This is effected in the following manner. In soil solutions, the acid metabolites dissociate to yield H^+ ions. The H^+ ion is, as a rule, incapable of existence as an individual entity, and promptly becomes bound via hydrogen bond to a water molecule to form the hydroxonium ion H_3O^+. The crystal structure of hypogene silicates can be transformed to that of clay minerals only via uptake of hydroxonium. Consequently, the rate at which acid metabolites are produced by terrestrial biota is an important factor in the hypergenesis of crystalline rocks and the buildup of crust of weathering.

5.3. Global Sulfur Cycle

Sulfur is a typical representative of the group of actively outgassed elements. At the same time, the access of sulfur to the atmosphere is more impeded as compared to inert gases or CO_2. This must be attributed to the following factors. Sulfur dioxide and hydrogen sulfide are of common occurrence among the gaseous sulfur compounds evolved with volcanic gases. The gases, during the mantle outgassing and their transit across the rock layers, become dissolved in underground waters. In this process, H_2S acts as a reducer of heavy metals to produce sparingly soluble sulfides, mainly iron disulfide (pyrite), whereas SO_2 binds in part to metals to yield likewise poorly soluble sulfates of calcium, barium, and strontium. By those reactions, a significant part of outgassed sulfur compounds become converted to hard rocks, among which pyrite FeS_2 is the most widespread. The average concentration of sulfide

(mostly pyritic) sulfur in the granitic layer of the continental crust is 0.064%, and that of sulfate sulfur, 0.04%. Based on the data of Ronov *et al.* (1976), one may accept that the sulfide sulfur mass in the granitic layer is $5.3 \cdot 10^{15}$ tons, and that of sulfate sulfur, $3.3 \cdot 10^{15}$ tons.

In magmatic fractionation of elements, sulfur and metals leave the silicate melt and enter the pneumatolytic hydrothermal fluids wherefrom they deposit accumulations of sulfides of iron, copper, zinc, lead, and other metals. It should be noted that the sulfide ore deposits account for thousandths of a percent of the mass of metal sulfides dispersed in the upper granitic layer of continental crust one kilometer thick.

Part of gaseous sulfur compounds diffusing through the Earth's crust, as well as volcanic sulfurous gases and gaseous-fluid emanations of land and deep-sea hydrothermal sources are delivered to the World's ocean and pedosphere. A substantial percentage of gases is taken up by bacteria to enter a specific microbiological cycle. Thus, the outgassed sulfur compounds on their route to the atmosphere must overcome a double-layer filter: a physicochemical one in the Earth's crust and a biogeochemical one on the surface of World's land and in the ocean.

The global sulfur mass transport in the biosphere is not associated only with the migration of gaseous compounds, but includes also the transport of water-soluble sulfurous compounds in surface and underground waters. The formation of water-soluble sulfurous species is associated with the hypergene transformation of insoluble sulfides, contained in rocks, into easily soluble sulfates. The metal sulfides in the hypergenesis zone are subject to hydrolysis and oxidation, with the resultant formation of sulfuric acid, insoluble hydroxides of iron(III), manganese(IV), as well as readily soluble sulfates. The formation of sulfates occurs also in soils by microbiological processes. The water-soluble sulfates are leached out of decayed rocks and are carried over from land in stream run-off. The SO_4^{2-} ion concentration in sea water is 2.7 g/liter. $3.7 \cdot 10^{15}$ tons of SO_4^{2-}, or $1.2 \cdot 10^{15}$ tons of sulfur has been accumulated in the World's ocean.

Sulfur is an essential component of living matter by virtue of its making part of the proteins in whose structure it plays an important role. The concentration of sulfur as a constituent of living matter of the World's land, mainly represented by higher plants, is relatively small, 0.34% of dry biomass (Bowen 1966).

In animals and bacteria, because of a high content of proteins in their biomass, the sulfur concentration is markedly greater. The C-to-S ratio in proteins is about 16, in carbohydrates, 80, in land plants, over 200, and in animals, about 70. The average sulfur content in the living matter of the ocean is 1.20% (on a dry weight basis). The C-to-S ratio in marine plants is about 50, not much different from that in terrestrial animals.

Sulfur found in the land biomass amounts to $8.5 \cdot 10^9$ tons, in the photosynthetic microorganisms of the ocean, to $0.07 \cdot 10^9$ tons, and in the oceanic consumers, to $0.05 \cdot 10^9$ tons. The sulfur concentration in the inanimate organic matter of land (forest litter, peat, humus) appears to be close to 0.5% by dry weight. If so, then the mass of sulfur in the organic matter of pedosphere is $15.5 \cdot 10^9$ tons.

Sulfur is an element actively taken up in the Earth's crust, hydrosphere, and living matter. For this reason, despite the intense sulfur outgassing from the Earth's interior, the natural levels of sulfurous gases in the atmosphere are rather low: the concentration for either H_2S, or SO_2 has been estimated to be about $2 \cdot 10^{-8}$%. The atmospheric content of both H_2S and SO_2 is highly variable and is influenced by anthropogenic factors; with allowance made for the latter, the overall amount of sulfur in the atmosphere is $14 \cdot 10^5$ tons.

It is to be inferred from the above that three major reasons determine the specificity of global sulfur cycle in the biosphere. First, sulfur is capable, assisted by microbiological processes, of forming gaseous compounds (SO_2, H_2S, and a number of others), which provides for its active involvement in the mass exchange between land, ocean, and atmosphere. Second, the sulfurous gases are prone to an easy conversion to readily soluble sulfates, which makes the aqueous migration of sulfur predominant over the gaseous migration. This is feasible owing to the prompt oxidation of reduced and suboxidized sulfurous gases by atmospheric oxygen followed by the formation of soluble sulfates which then are easily washed out of the atmosphere to be involved in the aqueous migration. Third, the water bodies and hydromorphic landscapes to which water-soluble sulfates are supplied abound in communities of sulfate-reducing bacteria. They decompose sulfates to produce hydrogen sulfide which, in turn, converts aqueous iron and other metals into sparingly soluble sulfides. These form deep-sea deposits providing thereby for a long-term preservation of tightly-bound sulfur masses.

Owing to the incessant loss of sulfur into deposits, the sedimentary shell has accumulated enormous amounts of this element. According to Ronov (1976), the average concentration of sulfide sulfur in sedimentary shell is 0.183%, its mass being $4.1 \cdot 10^{15}$ tons. The sulfate sulfur mass is $5.2 \cdot 10^{15}$ tons, and the total amount of sulfur is $9.3 \cdot 10^{15}$ tons.

At the same time, the granitic crustal layer contains $8.6 \cdot 10^{15}$ tons of sulfur. The dissolved oceanic sulfate sulfur having been taken into account ($1.2 \cdot 10^{15}$ tons), it becomes apparent that the biospheric content of sulfur is higher than the amount of this element that might potentially be extracted from a completely decayed granitic layer of the crustal continental block. The distribution of sulfur masses in the biosphere provides a convincing evidence that they have not been leached out of the decayed granitic layer, but rather brought into the biosphere through mantle outgassing.

The distribution of sulfur in the biosphere is as follows:

Reservoirs	Mass, $1 \cdot 10^9$ tons S
Atmosphere	0.0014
World's land:	
vegetable biomass	8.5
organic matter of pedosphere	15.5
Ocean:	
biomass of photosynthetic organisms	0.06
biomass of consumer organisms	0.09
soluble inorganic ions	1200000
Earth's crust:	
sedimentary shell	
sulfide sulfur	4100000
sulfate sulfur	5200000
granitic layer of continental block	
sulfide sulfur	5300000
sulfate sulfur	3300000

The living matter plays a very important role in the global geochemistry of sulfur in the biosphere, although this role, at least not inferior to that of carbon, shows up in quite a different manner. In the biogeochemical carbon cycle on land, the major factor is the interactive biotic activity of higher plants and edaphic microorganisms; by contrast, in the biogeochemical sulfur cycle, the interaction of various groups of bacteria comes to the foreground. Bacteria that synthesize organic matter may be regarded as producers, and those that decompose it, as destroyers (Zavarzin 1984). The interaction of these bacterial groups facilitates performance of minor biogeochemical cycles.

For example, the phototrophic purple bacteria oxidize hydrogen sulfide to yield sulfate as a metabolite:

$$H_2S + CO_2 \rightarrow [CH_2O] + SO_4^{2-}$$

A condition for continued activity of sulfur bacteria is the removal of a major metabolite, the sulfate ions. This provides for the activity of secondary anaerobic bacteria that utilize the sulfate ion for a substrate to yield the hydrogen sulfide metabolite. This reaction closes the minor sulfur cycle. It should be kept in mind, however, that the anaerobic sulfur cycle, as any biogeochemical cycle, is not a closed one in the strict sense of the term. The hydrogen sulfide formed is eliminated in two ways. First, sulfur becomes bound to produce black hydrated iron sulfides, known as hydrotroilite, which subsequently converts to pyrite and marcasite. Second, hydrogen sulfide migrates into the atmosphere. In the opinion of Zavarzin (1984), the secondary aerobic bacteria of sulfur cycle

produce most of hydrogen sulfide available in the atmosphere. The supply of this gas from volcanic sources is of minor importance.

The microbiological production of sulfurous gases is rather difficult to quantitate. According to Friend (1976), the annual supply of sulfur from ocean to atmosphere as produced by microorganisms is $48 \cdot 10^6$ tons. Part of this mass, in the form of suboxidized gases as SO_2, passes into solution ($25 \cdot 10^6$ tons), and the rest suffers complete oxidation to sulfates and become washed out by precipitation. Friend argues that the soil bacteria on land release in a gaseous form $58 \cdot 10^6$ tons of sulfur per year, of which $15 \cdot 10^6$ tons is taken up by vegetation, and $43 \cdot 10^6$ tons is oxidized in atmosphere to sulfates to be washed out with precipitation.

In addition, a significant mass of sulfates is blown away from the continental surface by the wind as dispersed particulate matter which makes part of airborne aerosols and then becomes precipitated to the surface. At present, this mass is amenable to a very rough estimate only. According to the data by Lein *et al.* (1988), a sulfur mass of $8 \cdot 10^6$ tons is annually involved in the aeolian emission to the atmosphere, with its subsequent precipitation.

A very intriguing discovery in biogeochemistry has been the effect of isotope fractionation by living organisms. The living cell components and extracellular metabolites are, as a rule, enriched in light isotopes. This phenomenon, dealt with in the foregoing Section on biogeochemical carbon cycle, is likewise no less spectacular in the biogeochemistry of sulfur. Four stable sulfur isotopes are known to occur in nature. The lightest of these, ^{32}S, is the most widespread with an abundance of 95.1%. The abundances of the others are: ^{33}S, 0.74%; ^{34}S, 4.2%; ^{35}S, 0.16%. Of practical interest are the two isotopes, ^{32}S and ^{34}S.

The relative abundance of these two isotopes may be estimated by the formula below:

$$\delta^{34}S = \left[\frac{^{34}S/^{32}S(\text{sample})}{^{34}S/^{32}S(\text{reference})} - 1 \right] \cdot 1000\%$$

As a reference, the troilite sulfur from the Cañon Diabolo meteorite has been accepted, with its ratio of $^{34}S/^{32}S = 0.0450045$. Any proportion of the two sulfur isotopes in natural objects may be expressed in terms of the $\delta^{34}S$ quantity whose value has a plus sign, if the $^{34}S/^{32}S$ ratio for a sample is higher over that of the reference, and a minus sign, if the opposite holds.

As has been established, the biogenous sulfur-containing compounds — both solid and gaseous — are enriched in the light isotope. The most marked effect has been observed in a reaction of biochemical reduction of sulfate to hydrogen sulfide as produced by *Desulfovibrio desulphuricans* bacteria. In this process, the reduced H_2S becomes enriched in light ^{32}S isotope, whereas the SO_4^{2-}

ions, not involved in the biogeochemical reaction, become residually enriched in ^{34}S isotope.

By virtue of microbiological sulfate reduction (a very widespread process in the biosphere), the sulfur mass, viewed from a standpoint of its relative isotope abundance, has become divided into two parts: (i) sulfur of biogenous sulfurous gases and their derivatives (sulfides) enriched in light isotope, and (ii) sulfate sulfur which, owing to the depletion of the light isotope, has increased its relative content of heavy ^{34}S isotope. Since sulfates are accumulated in the seas and oceans, the values of $\delta^{34}S$ in oceanic waters and evaporates are, respectively, 20 and 17, whereas the value of $\delta^{34}S$ for the sedimentary rocks, markedly abundant in biogeneous iron sulfide, is –12 The sulfur of H_2S as produced by sulfate-reducing microorganisms, has values of $\delta^{34}S$ reaching down to –43.

Various authors give substantially differing estimates for the sulfur masses involved in mass exchange in the systems "land-troposphere-land" and "ocean-troposphere-ocean". By way of example, Friend (1976) and Zehnder *et al.* (1980) have evaluated the sulfur release rate from the ocean surface in the form of biogenous sulfurous gases as $48 \cdot 10^6$ ton/year, and Lein *et al.* (1988), as $7 \cdot 10^6$ ton/year.

The major reason for such a large disparity resides in the difficulty of an experimental determination of sulfurous gas masses supplied from different sources. A point to be noted is that the sulfurous gases in the atmosphere are easily oxidized to sulfates which are readily washed out by precipitation. Therefore, if the annual mass of sulfates precipitated onto the ocean surface is known one can form an idea about the total of sulfur as supplied to the atmosphere in a different form and from a variety of sources. A similar approach may be applied to the World's land also.

Based on the annual precipitation over the World's ocean surface, is $411 \cdot 10^{15}$ liters, and the average mineralization of 10 mg/liter, one may reckon that the amount of dissolved salts, annually supplied to the ocean surface, is $4.1 \cdot 10^9$ tons plus 20% of this mass in the form of dry precipitation, $0.8 \cdot 10^9$ tons, totalling $4.9 \cdot 10^9$ tons, of which sulfur accounts for $0.29 \cdot 10^9$ tons per year. Besides, 10% of the total of salt mass air-borne over the Earth's aquatorium (see Section 3.8) is transported onto land. Therefore, about $0.31 \cdot 10^9$ tons of sulfur per year is supplied to the atmosphere over the ocean in a variety of ways (water dust entrainment, gas-bubble film burst discharge, biogenous and volcanic emanations of SO_2 and H_2S); of this, $0.83 \cdot 10^9$ tons in sulfate form (or $0.28 \cdot 10^9$ tons S) is precipitated into the ocean and somewhat lesser amount, $0.08 \cdot 10^9$ tons SO_4^{2-}, or $0.027 \cdot 10^9$ tons S is transferred to land.

Most territory of the World's land ($117 \cdot 10^6$ km^2) is drained via run-off streams into the World's ocean. All water bodies of this territory evaporate $62 \cdot 10^{15}$ liters

per year, which is then returned to land through precipitation. The average SO_4^{2-} concentration in terrestrial precipitation is about 5 mg/liter. Consequently, supplied from land to atmosphere and returned back is $0.310 \cdot 10^9$ tons of SO_4^{2-}, or $0.103 \cdot 10^9$ tons of S plus 20% of dry precipitation ($0.02 \cdot 10^9$ tons), which totals $0.123 \cdot 10^9$ tons of S per year. Besides, the ocean supplies $44 \cdot 10^9$ liters of precipitation to land via air masses, which makes an additional $0.03 \cdot 10^9$ tons of S per year.

The area of $32 \cdot 10^6$ km^2 of the World's land has no stream discharge to ocean. Confined to this territory is a tightly closed water cycle with a turnover of $7.5 \cdot 10^{15}$ liter/year and average SO_4^{2-} concentration about 30 mg/liter. Involved in this cycle is $0.225 \cdot 10^9$ tons of SO_4^{2-} per year, or $0.075 \cdot 10^9$ tons of S per year.

Thus, the annual supply of sulfur from the World's land surface is $0.198 \cdot 10^9$ tons, whereas its precipitated mass is larger by $0.03 \cdot 10^9$ owing to the transport from the ocean. Simultaneously, $0.162 \cdot 10^9$ tons of soluble sulfate sulfur are lost from land into the ocean with stream discharge.

At the sea (ocean) bed, the water-soluble sulfates undergo reduction to produce iron sulfides. The mass of sulfides formed defies exact determination, and the reported data show a 100-fold difference: $7 \cdot 10^6$ ton/year S (Zehnder *et al.* 1980) to over $100 \cdot 10^6$ ton/year S. According to Lein *et al.* (1988), the deposition rate of sulfide sulfur in the ocean is $0.111 \cdot 10^9$ ton/year, and that of sulfate sulfur appreciably smaller, $0.028 \cdot 10^9$ ton/year. The rate of bacterial sulfate reduction in the deep-sea bottom precipitates varies over a wide range of 0.001 to 1.8 mg of H_2S per 1 kg of precipitated material per day.

Turning to different sources of sulfurous gases supply to the biosphere, it must be noted that the release of H_2S on land and in the ocean is estimated to be tens of million tons of sulfur per year. The emission of hydrogen sulfide is more active in sea coast shallows and in boggy landscapes. As noted earlier, H_2S and SO_2 undergo a fast oxidation in the atmosphere to be converted to the sulfate form. There has been reported evidence, however, that part of SO_2 is solubilized in sea water and also taken up by land plants and by soil.

It is noteworthy that substantial amounts of various sulfur compounds are delivered through hydrothermal sources. Zehnder *et al.* (1980) have estimated that $129 \cdot 10^9$ tons of sulfate sulfur per year are supplied in such a manner. The sulfur emission in volcanic eruptions is much lower and is variously estimated as 2 ton/year (Friend 1976) to 28 ton/year (SCOPE-21, 1983).

Along with the important role of chemolithotrophic bacteria in the global sulfur mass exchange, the contribution from photosynthetic bacteria is also substantial. One may presume, starting from the productivity of the terrestrial vegetation intact by man and its average dry-weight sulfur content of 0.34%

(Bowen 1966), that some $0.59 \cdot 10$ tons of sulfur is annually involved in the biological sulfur cycle on land. The average sulfur concentration in oceanic photosynthetic organisms is appreciably higher (1.2%) over that in land plants (Bowen 1966). Accordingly, $1.32 \cdot 10^9$ tons of sulfur per year are involved in the biological cycle in the ocean.

The major features of the present-day sulfur mass exchange appear to have evolved over 0.5 billion years ago. As shown by the foregoing material, the global sulfur cycle in the biosphere is to a significant extent determined by biogeochemical processes. Simultaneously, both the global cycle pattern and sulfur mass distribution suffered change as the surroundings were gradually transformed by the biotic activities of organisms.

The studies of isotope composition of differently aged sulfur deposits have led to interesting results. As has been established, the $^{32}S/^{34}S$ ratio varied but little in the deposits aged more than 2 billion years, indicating a low activity of sulfate-reducing and sulfur bacteria. In the later periods, strong fluctuations in the isotope ratio have been recorded which is suggestive of the selective uptake of light ^{32}S isotope by living organisms. About 1.7 billion years ago, heavy layers of marine sulfates (gypsum and anhydrite) started to form. Apparently, this was associated with an ever-increasing supply of oxygen owing to the activity of cyano bacteria within a period of 2.8-1.7 billion years ago. According to Schidlowski (1980), 38% of the total of oxygen that was produced during the entire period of geological history had become bound in heavy sulfate deposits (gypsum and anhydrite). The gypsum deposits are enriched in heavy ^{34}S isotope, which is suggestive of a high activity of the ancient bacteria that had taken up a significant mass of light isotopes, ^{32}S included. Owing to this, the gypsum rocks became residually enriched in heavy ^{34}S isotope.

The global sulfur cycle is highly open, which is manifest in the incessant removal of large "excess" sulfur masses from the migratory fluxes in the form of deposited iron sulfides and calcium (and in part magnesium) sulfates. Owing to this elimination, the concentration of sulfurous gases in the ocean and in the atmosphere is maintained at a very low level. However, sulfur is a major component of the gases released from the Earth's interior. Taking into account the mass of sulfur contained in various forms in the sedimentary shell and in the World's ocean, one comes to the conclusion that at least $10.5 \cdot 10^{15}$ tons of sulfur was involved in the processes occurring in the biosphere during the entire period of its existence.

The release into the atmosphere, pedosphere, and natural waters of sulfur compounds arisen from the activities of man ranks among the strongest anthropogenous environmental impacts.

The main technogenous influx of sulfur into the atmosphere is caused by the emission of sulfurous gases as produced by the combustion of fossil fuels and metallurgical production. Major sources for contamination of natural waters

Table 5.5. Mass Transport of Sulfur in Biosphere

Mass exchange process	Mass of sulfur, $1 \cdot 10^6$ tons per year
World's land	
Biological cycle (photosynthesis-degradation of organic matter)	590
Mass exchange between land and troposphere:	
release of biogenic gases from pedosphere to troposphere	210
washout of oxidized gaseous compounds from troposphere	230
Stream loss:	
as component of solubilized inorganic ions	162
in soluble organic matter	2
in suspended organic matter	1
Transport of air-borne $[SO_4]^{2-}$ ions of oceanic origin to land	22
World's ocean	
Turnover of planktonic photosynthetic organisms	1320
Release of gaseous sulfur compounds to troposphere	310
Washout of soluble oxidized gaseous compound from troposphere	290
Deposited sulfide sulfur	100
Deposited sulfate sulfur	30
Technogenic emission to troposphere	110
Liquid industrial and domestic wastes	60

with soluble sulfur compounds are the run-off of fertilizers and the industrial wastes from chemical plants.

Over 95% of the technogenous sulfurous gas discharge is accounted for by SO_2 and its derivatives SO_3 and H_2SO_4 which induce metal corrosion and produce detrimental effect on plants, animals, and humans. According to Altshuler (1980), in the mid-1970s, $120 \cdot 10^6$ tons of SO_2 and $4\text{-}5 \cdot 10^6$ tons of H_2S were annually supplied to the atmosphere from a variety of sources. The current prognosis predicts an emission rise as high as $300\text{-}450 \cdot 10^6$ ton/year by the year 2000. In the atmosphere, SO_2 is rapidly converted to SO_3 and then to H_2SO_4. The latter, on its interaction with ammonia that is always present in the troposphere, produces ammonium sulfate. Under definite conditions, part of SO_2 is washed out by precipitation to be taken up by plants and soil. Most SO_2 becomes oxidized to SO_4^{2-}, the most widespread species among the

precipitable sulfur-containing compounds. The total amount of sulfur annually supplied to the atmosphere from industrial sources is about $100\text{-}110 \cdot 10^9$ tons S.

The run-off of mineral sulfur-containing fertilizers, $20\text{-}30 \cdot 10$ ton/year of S, contributes to the mass transport of water-soluble sulfur compounds, in particular, to the continental run-off. About the same amount of sulfur is supplied in the wastes from chemical, mining, and metallurgy industries.

The data, summarized in Table 5.5, show that the technogenous emissions of sulfur compounds into the environment do not impair the balance of sulfur masses involved in the global cycle. Simultaneously, the sulfur compounds, discharged in industrial and domestic wastes, produce a detrimental effect on the biota of vast regions endangering thereby the normal function of the most important link of the biosphere. The large-scale discharge of SO_2 into the atmosphere is responsible for the so-called "acid rains" that extend far beyond the industrial areas. The water-soluble sulfur compounds in industrial and domestic wastes afflict, on a world-wide scale, the ecosystems of large intracontinental water bodies and shelf seas. The control over the hazardous transport of technogenous sulfur compounds has at present come to the foreground of urgent problems facing the civilized world.

5.4. Global Nitrogen Cycle

Nitrogen is one of the elements that became an individual component of the gas phase at the early stages of the Earth's buildup and was produced by shock outgassing. Further, the emission of nitrogen from the Earth's interior continued as gas stream eruptions from volcanos and hydrothermal sources. The gaseous molecular nitrogen, owing to its chemical inertness, is the most stable form for the occurrence of this element. For this reason, N_2 from the very beginning was being accumulated in the atmosphere, in contrast to chlorine that passed in a soluble form into the ocean waters, or to carbon that was deposited as an insoluble component in the carbonate rocks. At the present time, the emission of gaseous nitrogenous compounds from the Earth's interior into the atmosphere appears to be close to $1.0 \cdot 10^6$ ton/year.

The major nitrogen mass in the form of N_2 amounting to $3870000 \cdot 10^9$ tons is found in the atmosphere. Gaseous N_2 is partially dissolved in the water of World's ocean. At a state of equilibrium with the atmospheric gases, the ocean contains $115000 \cdot 10^9$ to $20000 \cdot 10^9$ tons of N_2 dissolved in its waters.

In the ocean, nitrogen occurs also in a solubilized ionic form, and as a constituent of dissolved and suspended disperse of organic matter. The mass of nitrogen occurring in the form of soluble salt ions NH_4^+, NO_2^-, and NO_3^- amounts to about $685 \cdot 10^9$ tons.

The average concentration of nitrogen in the living matter of the World's land, mostly represented by green vegetation, is estimated by various authors as 0.6% (Bazilevich 1974) to 3% (Bowen 1966) by dry weight. A significant part of the terrestrial plant biomass is confined to the wood of tree trunks mostly composed of cellulose and lignin. For this reason, we have adopted for our calculations the average nitrogen content in the dry biomass of plants to be 1%. Perhaps, this value may happen to be slightly overestimated. Still, the annual growth of terrestrial vegetation, mostly the vegetative organs of plants, contains more proteins than the overall phytomass does. For this reason, we have adopted the average nitrogen content in the annual growth to be equal to 2%, in accordance with the data by Romankevich (1988). The above having been taken into account, one may presume that the vegetable biomass of the World's land, intact by human activities, contained about $25 \cdot 10^9$ tons of nitrogen. In the organic mass of the pedosphere, the average nitrogen concentration is close to 3-4%, the overall nitrogen mass being about $110 \cdot 10^9$ tons. Nitrogen, occurring in the pedosphere in the form of salts, mostly nitrates, is much less; its mass escapes exact determination.

The nitrogen concentration in oceanic photosynthetic organisms has been estimated as 4.5% (Basilevich 1974) to 8.2% (Romankevich 1988), on average, 6% of dry organic matter, or $0.20 \cdot 10^9$ tons of nitrogen. In the consumer organisms, given the average nitrogen concentration of 7%, the nitrogen mass is $0.32 \cdot 10^9$ tons. The overall nitrogen mass in the organisms of the ocean is $0.52 \cdot 10^9$ tons. The dissolved organic matter of the ocean contains 6% of nitrogen by dry weight (Vinogradov 1987) which corresponds to $252 \cdot 10^9$ tons of nitrogen; in the suspended organic matter, the nitrogen mass is about 10 times less. The total of nitrogen in the dead organic matter of the ocean is about $0.3 \cdot 10^{12}$ tons.

In the granitic crustal layer, the nitrogen concentration is 0.002%, the overall mass of this element being $165 \cdot 10^{12}$ tons. In the sedimentary shell, the nitrogen is confined to organic matter. The mass of the latter is about $30 \cdot 10^{15}$ tons (C_o mass = $15 \cdot 10^{15}$ tons). According to Degens (1965), the nitrogen concentration in dispersed organic matter is close to 2%. One may presume, on this basis, that the nitrogen mass in the sedimentary shell amounts to about $0.6 \cdot 10^{15}$ tons. It follows from the above data that in the sedimentary shell, the nitrogen mass is 3 times, and in the atmosphere, 23 times the nitrogen mass in the granitic layer of the lithosphere.

Consequently, the overall amount of nitrogen available in the biosphere cannot be explained as having arisen from the decayed granitic layer. Apparently, the bulk of biospheric nitrogen has been supplied through degassing. At the present time, the amount of gaseous nitrogen emitted into the atmosphere from the Earth's interior has been estimated to be about $1 \cdot 10^6$ ton/year. In the geological past, the emitted nitrogen mass might have been even larger. The inventory of nitrogen distributions in the biosphere is listed below.

Reservoirs	Mass, $1 \cdot 10^9$ tons N
Atmosphere, N_2	3870000
World's land:	
vegetable biomass (intact by man)	25
organic matter of pedosphere	110
Ocean:	
biomass of photosynthetic organisms	0.20
biomass of consumer organisms	0.32
organic matter (dissolved and suspended)	300
soluble salt NO_3^- ions	685
dissolved gaseous N_2	20000
Earth's crust:	
sedimentary shell	600000
granitic layer of continental block	165000

Thus the major supplier of nitrogen to the biosphere is the Earth's interior, and the major accumulator of nitrogen is the atmosphere, or, more exact, troposphere. However, the atmosphere should not be regarded as a closed reservoir that has functioned for over 4 billion years merely to receive and store the gaseous nitrogen compounds. Compositionally, the atmospheric nitrogen is incessantly renewed owing to the cyclic mass-exchange processes involving the atmosphere, World's land, pedosphere, ocean, and atmospheric precipitations.

The modern structure of the global nitrogen mass-exchange cycle is quite complicated and is constituted by a number of interdependent minor cycles. The general trend of the cycle performance consists in the migration of nitrogen masses between the major accumulator, the atmosphere, and other reservoirs of smaller scale, the pedosphere, living matter, and ocean. One of the minor cycles is characterized by photochemical reactions occurring in the troposphere. Along with N_2, other gaseous nitrogen compounds, NH_3, N_2O, NO, NO_2, are continually supplied to the atmosphere. Their storage is precluded because of photochemical reactions. The photochemical dissociation of water vapors yields hydrogen (which dissipates into outer space) and a strong oxidant OH^-. The OH^- radical reacts with NO and NO_2 to produce nitrous and nitric acids and, subsequently, salts, nitrites and nitrates. Along with the nitrogen oxides, present in the atmosphere is a reduced nitrogen compound, ammonia. In an oxygen-containing atmosphere, ammonia reacts with sulfur oxides to yield hydrogen ammonium sulfate, NH_4HSO_4. This compound, similar to nitrites and nitrates, is easily washed out by rainfall.

Presumably, the primary migration cycle of nitrogen consisted of a photochemical conversion of all gaseous nitrogen compounds (except N_2) to oxidized soluble forms followed by their removal from the atmosphere. At the earliest

stages of the geological history of the Earth, this cycle included the activity of the most ancient group of living organisms, the bacteria, which gradually led to a profound change of the entire structure of global nitrogen mass exchange. At present, the photochemical reactions are likewise involved in the elimination of nitrogen from the atmosphere; however, the biogeochemical activity of bacteria is predominant in this process.

A remarkable property of nitrogen is its ability to persist in a number of valent states. This fact is of no minor importance for the biogeochemical processes. The organisms, through converting nitrogen from one form to another and through changing its state of valency, gain energy for their biotic activity. Perhaps, this circumstance was not the least one in rendering nitrogen a very essential constituent of proteins.

Nitrogen by right is called the element of life. A semantic curiosity is that nitrogen in French is referred to as azote, the term coined by Lavoisier and signifying "not supporting life". The occurrence of nitrogen in the pedosphere in the forms accessible to higher plants is a condition providing for the production of the vegetable biomass, which is in essence the mass of living matter of the Earth. The uncommonness of the situation is that most of this element present in the atmosphere in a chemically inert form N_2 is inaccessible to the major producers, green terrestrial plants. However, the chemical inertness of nitrogen signifies by no means its geochemical stability. There are known species of bacteria capable of activating the molecular nitrogen and binding it into chemical compounds. This process is commonly referred to as nitrogen fixation.

In the organisms, most of nitrogen occurs either in the form of compounds whose constitutive element is the amino group NH_2, or in the form of ammonia. In the course of biochemical fixation, the N_2 molecule becomes split into nitrogen atoms which, on their reaction with hydrogen, form ammonia. This process is assisted by the enzyme nitrogenase. Ammonia and the NH_4^+ ion are taken up by the plant roots to make part of the amino acids.

The nitrogen fixation is effected by specialized bacteria of the family *Azotobacteracea* and, under definite conditions, by blue-green algae. The nitrogen-fixing nodule bacteria, symbiotic with leguminous plants, are the most productive ones. The mass of nitrogen that has been fixed from the air by soil bacteria prior to human activities is estimated by various authors as 30-40 to $200 \cdot 10^6$ tons per year. At the present time, additional sources of nitrogen fixation arise from the commercial cultivation of leguminous plants (about $20 \cdot 10^9$ ton/year) and from the uptake of nitrogen from the air for industrial purposes (over $60 \cdot 10^6$ tons per year).

Prior to the human interference with the global nitrogen cycle, the amount of bacterially fixed nitrogen was roughly counterbalanced by the nitrogen

release from dead organic matter and its supply, after a series of conversions, to the atmosphere in the form of gaseous compounds. This chain of conversion is effected through the agency of interdependent bacterial processes occurring in the soil. Of these, the first is ammonification, or the microbiological conversion of the nitrogen of organic species (mostly, amino acids) into the ammonium ion or ammonia. The degradation of organic matter proceeds under aerobic conditions and is attended by an active production of CO_2. Ammonia undergoes the following transformation. Under aerobic conditions, nitrification takes place, which is the conversion of ammonia to the nitrite ion by some bacteria, and then to the nitrate ion, by others. Under anaerobic conditions denitrification processes develop, with the resultant reduction of nitrates and nitrites to nitrous oxide or to gaseous molecular nitrogen. At the final stage, the molecular nitrogen, subjected to a variety of biochemical conversions, returns to the atmosphere. The estimates of annual nitrogen production by bacterial denitrification vary over a wide range of 40-50 to $350\text{-}400 \cdot 10^6$ tons.

The nitrogen mass as fixed by soil bacteria is estimated within a range of 44 to $200 \cdot 10^6$ tons per year. At the present time, the denitrification production which was, prior to human activities, counterbalanced by the bacterial fixation production, is slightly in excess of the latter. The amount of nitrous oxide as produced by denitrification is several times less than the N_2 mass.

The above cycle "molecular nitrogen fixation-ammonification of dead organic matter-nitrification-denitrification" is of pivotal importance for the global nitrogen mass exchange insofar as this cycle provides for the major import of nitrogen from its main reservoir, the atmosphere. Moreover, a certain amount of atmospheric N_2 becomes oxidized by electric discharges to be washed out in the form of NO_3^- ion; however, it is appreciably smaller than the mass of biologically fixed nitrogen and ranges within 10 to $40 \cdot 10^6$ tons per year.

The cycle involving the bacterial fixation of nitrogen and its subsequent conversion is closely related to another potent cycle of this element. Large masses of nitrate and ammonium nitrogen are entrained from the pedosphere into a biological cycle involving the activity of photosynthetic plants and microorganisms that digest the plant remains. Given the average nitrogen concentration in the annual growth of land vegetation as 2%, one arrives at an estimate of $3.5 \cdot 10^9$ tons per year of nitrogen involved in the biological cycle between soil and vegetation unaffected by the human factor.

Most of this mass returns to the soil as components of plant remains and enters into microbiological processes whose final result is the breakdown of organic matter; nitrogen converts to ammonium and nitrates accessible to plants and becomes taken up by plants. Part of plant-assimilated nitrogen is ingested by animals to be finally returned to the soil. Part of nitrogen is removed from the biological cycle and becomes stored in the dead organic matter. This peculiar

reserve of nitrogen in the forest litter, peat, and humus is permanently maintained in the pedosphere and imposes a kind of restriction on the biological cycle on land. Forest wildfires are substantial contributors of nitrogen oxides to the atmosphere and account for 10 to $200 \cdot 10^6$ tons of additional annual supply of nitrogen.

In the ocean, the processes of conversion and migration of nitrogen compounds are basically the same as on land, although in different proportion. The life cycles of oceanic photosynthetic organisms are of much shorter duration than those on land. For this reason, the annual nitrogen turnover in the oceanic photosynthetic organisms is much higher. Moreover, the nitrogen concentration in the marine organisms, 6% of dry biomass (Romankevich 1988; Bowen 1966), is higher than that in the terrestrial organisms. The productivity of photosynthetic organisms in the ocean, $100 \cdot 10^9$ ton/year of dry biomass, indicates that the biological cycle of these organisms involves about $6 \cdot 10^9$ tons of nitrogen per year. Simultaneously, the biological fixation of nitrogen in the ocean is two times less, and the denitrification, almost 10 times less than that on land.

The migratory masses, driven by biological processes, play a crucial role in the global nitrogen mass exchange. Still, a certain amount of this element migrates via other routes.

The concentration of inorganic (nitrate and ammonium) nitrogen in rainfall on the territories of the Northern Hemisphere unaffected by human activities is close to 0.5 mg/liter. Therefore, the initial supply of nitrogen in the form of water-soluble inorganic species to the World's land surface was about $50 \cdot 10^6$ ton/year. At the present time, the amount of water-soluble nitrogen compounds supplied to land from the atmosphere has increased substantially (about 1.5 times) owing to the industrial nitrogen emission and to the deflation of nitrogenous fertilizers applied to the soil.

The nitrogen mass annually washed out by rainfall is replenished by the tropospheric soluble compounds as produced via conversion of gaseous nitrogen compounds of pedo-microbiological origin and, in part, as supplied by Earth outgassing.

A substantial mass of nitrogen is taken up by surface waters from the pedosphere and carried away as stream loss into ocean. The average NO_3^- ion concentration in uncontaminated water streams is 1 mg/liter (Livingston 1963) or, converted to nitrogen, 0.225 mg/liter. The loss of inorganic nitrogen from land is $9.2 \cdot 10^6$ ton/year. The nitrogen migrates in stream waters as a constituent of soluble and suspended organic matter. The average concentration of the former is close to 7 mg/liter, and of the latter, to 5 mg/liter. The average nitrogen percentage in the organic matter of stream water is 3%; consequently, the annual loss of nitrogen in soluble organic matter is $8.6 \cdot 10^6$ tons, and in suspended organic matter, $6.1 \cdot 10^6$ tons. The overall nitrogen loss is $24 \cdot 10^6$ ton/year. Some

researchers are of the opinion that the average concentration of inorganic nitrogen in stream run-off is 0.5 mg/liter, and of organic 1 mg/liter (Chemistry of Ocean 1979). Based on the above data, the overall transport of nitrogen by the World's land streams has been estimated as $61 \cdot 10^9$ ton/year.

The natural concentration of soluble inorganic nitrogen compounds in the precipitation over the World's ocean is likely to be 0.2 mg/liter N. Accordingly, the nitrogen mass as precipitated onto the ocean surface is about $82 \cdot 10^6$ ton/year.

Considering the evolution of global nitrogen mass exchange over time, one may presume an initially simple pattern for the mass-exchange cycle. The cycle was conditioned by the supply of outgassed nitrogen compounds which, by the action of tropospheric photochemical reactions, became converted to water-soluble nitrates and sulfate of ammonium to be then washed out by rainfall. With the gradual and ever-increasing participation of living organisms (bacteria), the cycle became more complex and finally included all links of the microbiological cycle: fixation of molecular nitrogen-ammonification-nitrification-denitrification. These microbiological processes have provided conditions for the emergence of terrestrial plants with a system of soil nutrition. Apparently, the ancient bacterial biocenoses, confined to shallow and water-logged silting deposits, were prototypes of modern soils. In further course, with the colonization of the land territories by terrestrial vegetation, there arised the "large" biological nitrogen cycle, and the pedosphere started to form as a major regulator of the global nitrogen cycle. The photosynthetic organic matter has served as a basis for the buildup of a biological nitrogen cycle with the participation of animals.

Nitrogen does not form insoluble compounds that might have been components of the World's ocean sedimentation. The zoogenic accumulations of sodium nitrate (guano) are rather small. Most nitrogen as supplied to the sedimentary shell makes part of the organic matter. One may presume, starting from the data by Ronov (1976), that the annual sedimentation losses of organic carbon are about $10 \cdot 10^6$ tons, which corresponds to roughly $20 \cdot 10^6$ tons of dry organic matter. Assuming its nitrogen concentration as an average of the nitrogen contents in the vegetations of land and ocean, i.e. 5%, one may estimate, on a very tentative scale that, prior to human activities, the loss of nitrogen into sedimentation was $1\text{-}2 \cdot 10^6$ ton/year. Presumably, this value does not differ significantly from the annual mass of nitrogen outgassed from the Earth's interior.

Appreciable masses of molecular nitrogen, like those of other tropospheric gases, take part in the physical gas exchange with the World's ocean. Depending on physicogeographical conditions, 8.4 to 14.5 mg/liter of N_2 can be dissolved in sea water. According to Vinogradov (1967), one liter of oceanic water contains 13 cm^3 of dissolved N_2; the total of the World's ocean contains $18 \cdot 10^6$ km^3 of N_2, which makes up almost 1.5% of the ocean volume. This enormous

Table 5.6. Nitrogen Migration in Biosphere

Mass-exchange process	Nitrogen mass, 10^6 tons per year
World's land	
Higher plant cycle (photosynthesis–destruction of organic matter)	300*
Bacterial cycle	
nitrogen fixation	40-200
denitrification	40-50 to 350-400
Nitrogen cycle involving animals	90-190
Emission into atmosphere from forest wildfires	10-200
Wash-out from atmosphere by rainfall	50
River stream loss	24-61
Outgassing from the Earth's interior	1-9
World's ocean	
Photosynthetic plankton cycle	6000
Bacterial cycle	
nitrogen fixation	1-20
denitrification	0-330
Wash-out from atmosphere by rainfall	82
Sedimentary deposition	1-9
Technogenic contributions	
Industrial consumption of nitrogen	60
Emission of nitrogen into environment through domestic and industrial wastes	10-20

* Agricultural crops included

amount of dissolved nitrogen persists in a state of dynamic equilibrium with the atmospheric nitrogen. Dissolved in the ocean water are also other gaseous nitrogen compounds, primarily, NH_3; however, both their contents and migration defy exact estimation.

The nitrogen cycle has become strongly affected by human activities. The most significant change in the global nitrogen cycle is associated with the industrial utilization of molecular nitrogen from the atmosphere taken for the production of nitrogen fertilizers and their application to the soil. The mass

of nitrogen used for industrial needs exceeds now $60 \cdot 10^6$ tons per year. No less important appears to be the ever-growing intensification of biological fixation of nitrogen through the wide use in agriculture of the leguminous crops, symbiotic with the nitrogen-fixing bacteria. In 1970, about $15 \cdot 10^6$ tons of nitrogen was consumed in such a manner; at present, the amount of nitrogen used for commercial needs has increased substantially.

The industrial fixation of nitrogen appears to be the most strong human impact on the natural global cycles of mass exchange of chemical elements in the biosphere.

Moreover, a significant quantity of nitrogen (about $40 \cdot 10^6$ tons per year) in its oxidized forms is supplied to the atmosphere as industrial gases and combustion products from fossil fuels, also to the hydrosphere as domestic and industrial wastes. The effects of contamination on biogeochemical processes will be dealt with below in a separate chapter.

It should be noted that a study of nitrogen mass exchange meets with much difficulty. For this reason, the quantitative estimates of separate migratory fluxes and nitrogen cycles as reported by various authors differ greatly among themselves. The relevant data are listed in Table 5.6 featuring the major trends of nitrogen mass exchange in the biosphere.

5.5. General Characterization of Cycles and Mass Distribution of Outgassed Elements

The mass-exchange cycles for carbon, nitrogen, sulfur, and chlorine share a number of common features.

First, these cycles, starting from their origin, are maintained by the continuous supply of gas masses. According to our estimates, the following quantities of elements have been outgassed from the Earth during the entire period of its geological history (in 10^{15} tons): carbon, 96.04; chlorine, 33.0; sulfur, 10.5; nitrogen, 4.47; also water, 1600. The relevant data as reported by other authors, although numerically somewhat different, are of the same order.

Second, the gas elements are of decisive importance for the living organisms which are mainly composed of these elements. The very existence of life as a planetary phenomenon would have been impossible without a permanent supply of the gases to the environment. The available facts provide evidence that life and the processes that occur in the Earth's interior are intimately related. The evolutionary history of life reflects, in a definite manner, the endogenous processes. This is spectacularly exemplified by the discussed dependence of the production of biological processes, in particular, of the mass of photosynthetic organic matter, on the amount of volcanic CO_2 released.

Table 5.7. Mass Distribution of Chemical Elements as Supplied to the Biosphere Through Earth Outgassing

Reservoir	Element mass, $1 \cdot 10^9$ tons			
	C	N	S	Cl
Atmosphere	668	3866000	0.001	—
World's land:				
vegetation	1150	25	8.5	5.0
	(120)	(56)	(8)	(1.5)
organic matter of pedosphere	1550	110	15.5	0.3
	(166)	(246)	(15)	(0.09)
Ocean:				
photosynthetic organisms	4	0.52	0.15	0.03
	(0.4)	(1.1)	(0.1)	(0.01)
soluble organic matter	2100	300		
	(218)	(617)		
solubilized inorganic ions	38500	685	1200000	26500000
Sedimentary shell	96000000	600000	9300000	6500000
Element mass in biosphere, $1 \cdot 10^{15}$ tons	96.04	4.47	10.50	33.0

Values in parentheses account for $1 \cdot 10^{-5}$% of the total element mass in biosphere.

Third, the global mass-exchange processes of outgassed elements have become profoundly modified by the activity of organisms. The organisms, owing to their propensity to adaptation and variability, produced slow and irrevocable changes in the environmental geochemistry. This made the primary abiogenous cycles transform gradually into biogeochemical cycles of more complicated structure.

Along with their common features, the global mass-exchange cycles for each element are clearly distinct. The gas elements take an active part in biological processes, having alternate involvement and elimination from life cycles. In doing so, the elements adopt various forms for their occurrence which entails a change in their mass distribution in the biosphere.

The data, presented in Table 5.7, show that 99.9% of the mass of carbon outgassed as CO_2 was a constituent of the products of biotic activity of organisms: 15.6% in the form of organic matter dispersed in the sedimentary shell, and 84.3% as components of biogenous carbonates. Concurrent processes

were the cleavage of liquid water molecules and the release of free oxygen, which has gradually brought about drastic alterations in the geochemical state of the outer Earth's shell and its transformation into the recent biosphere.

A significant part of the sulfur mass is also found in sedimentary deposits, although with a smaller percentage than that of carbon. The sedimentary shell contains 88.6% of total sulfur, whereas 11.4% occurs in the ocean as soluble sulfates. In the sedimentary shell, the sulfate sulfur (55.9%) is predominant over the sulfide (44.1%). Thus, the oxidized forms of sulfur dominate in the biosphere.

The forms for the occurrence of chlorine were to a lesser extent subject to biogeochemical metamorphosis than other gas elements. Most chlorine is stored as Cl^- ions in the World's ocean, 80.3%; the rest of 19.7% is found in the sedimentary shell.

Most of nitrogen (86.5%) is involved in the system of biological cycles and is found in the atmosphere; its content in the sedimentary shell is a mere 13.4%.

To conclude this Chapter, we wish to emphasize that despite the negligible mass of living matter with respect to the total mass of biosphere (with elemental contents of the order of a few millionth parts), the activity of organisms was a major factor in the extant mass distribution of outgassed chemical elements. It should be inferred, therefore, that the living matter plays the role of a geochemical separator of elements rather than that of a reservoir. The biogeochemical fractionation encompasses not only elements, but partly their isotopes also. The components of a living cell and its extracellular metabolites become enriched, as a rule, in light isotopes of carbon and sulfur, and the residual products, in heavy ones.

6 Biospheric Cycles of Elements Mobilized from the Earth's Crust

Most chemical elements became involved in migration owing to the hypergene metamorphosis of the crustal alumosilicate matter. Goldschmidt (1937) performed tentative calculations of the elemental mass differentiation in the sedimentary shell starting from a concept that the elements were extracted from the crustal surface of the whole Earth. In reality, the elements were extracted only from the World's land rocks, whereas the seas and oceans serve as sinks for the elements that have been carried away from land as sediments and soluble compounds.

According to the refined and updated determinations (Ronov *et al.* 1976), the upper granitic layer of the crustal continental block has a mass of $8.24 \cdot 10^{18}$ tons, and the sedimentary shell (the effusives excepted), that of $2.4 \cdot 10^{18}$ tons. The mass of soluble salts in the World's ocean amounts to about $50 \cdot 10^{15}$ tons as estimated from the average sea water salinity of 35%. The mass total of granitic layer and sedimentary shell may be taken, by convention, for 100%. Therefore, during the period of geological history, about 20% of the upper layer of the crustal continental block was lost into the World's ocean. Of that mass, most made part of sedimentary rocks; about 0.5% is soluble inorganic compounds found in the seas and oceans. A certain amount of rock matter, metamorphosed by hypergenesis (eluvial crusts of weathering and redeposited weatherworn products) is located on land. No estimate of those masses is as yet available.

6.1. Global Calcium Cycle

Calcium is ranked among the major elements of the Earth's crust; its crustal abundance is 3.6%. The calcium content decreases from depth upward to the "granitic" layer of lithosphere. In the basaltic layer, its average concentration is 5.8%, and in the granitic, 2.7%. Calcium forms deposits at the early stages of magma crystallization; it is also contained in the residual (after crystallization) solutions. The high crustal calcium content provides for the occurrence of diverse minerals (a total of 385 species), of which a half account for deep-layer silicates. Simultaneously, the Ca^{2+} cation, because of its large size, is incapable of entering the structure of hypergene silicates. For

this reason, in weathering and metamorphosis of deep-layer silicates to clay minerals, large amounts of this element become liberated. The water-soluble calcium compounds, most commonly bicarbonate $Ca(HCO_3)_2$, are supplied to the natural waters and migrate therein to the ocean. Although this process has been developing for over 2 billion years, the actual calcium concentration in oceanic water is merely 30 times that in stream waters. This is due to the limited solubility of calcium carbonate and, specifically, to the active calcium uptake by planktonic organisms followed by calcium deposition as pellets. These processes have facilitated the profuse accumulation of calcium as a component of massive layers of limestone, dolomite, marl, calcareous clay, and other species.

According to Ronov (1976), the average CaO concentration in sedimentary layer is 15.91%, and in crustal granitic layer, 2.71%. The calcium mass in sedimentary shell is $272.8 \cdot 10^{15}$ tons, and in granitic layer, $222.8 \cdot 10^{15}$ tons. It is to be inferred from the above, that the quantity of calcium in sedimentary shell is higher than its content in the granitic layer of the lithosphere. The imbalance of calcium mass in the biosphere poses before the geochemists a problem to be resolved.

Calcium plays a pivotal role in the physiology of organisms. In plants, it is involved in the carbon and nitrogen metabolism; in animals, it is essential for the buildup of their inner and outer skeleta. Calcium takes part in a vast variety of physiological processes, in particular, blood coagulation. The average calcium concentration in terrestrial vegetation falls, according to various authors, within the range of 0.9% (Bazilevich 1974) to 1.8% (Bowen 1966). The mass of calcium contained in the living matter of land is $22.5–45 \cdot 10^9$ tons. This quantity is three orders of magnitude higher than that contained in the biomass of oceanic photosynthetic organisms ($34 \cdot 10^6$ tons). Given the average calcium concentration in dead organic matter about 0.5%, one may presume that the calcium mass contained in plant remains, peat, and humus is $15 \cdot 10^9$ tons, that is, of the same order as that in the entire living matter of the World's land. Conventionally, the average calcium concentration in the soluble organic matter of the ocean may be accepted as equal to 0.5% of dry matter, which makes up the mass of the element of $20 \cdot 10^9$ tons.

Owing to the dynamic equilibrium between the atmospheric carbon dioxide and the oceanic HCO_3^- and CO_3^{2-} anions, an enormous mass of solubilized calcium cations is contained in the ocean. This mass is four orders of magnitude higher than the mass of the element bound in the living and dead matter of the planet. The average calcium concentration in the ocean is 408 mg/liter, the overall mass of the element being $559 \cdot 10^{12}$ tons.

For the global calcium mass exchange the biological cycle and the aqueous migration of ions within the "land-ocean" system are of prime importance.

Involved in the biological cycle on land is $1.5 \cdot 10^9$-$3.1 \cdot 10^9$ tons per year, an average being $2.3 \cdot 10^9$ tons per year; in the primary biological production of ocean, this quantity is two times less, i.e. $1.1\,10^9$ tons per year. Thus, calcium should be viewed as a typomorphic element for the terrestrial living matter. The planetary turnover of calcium, involved in the biological cycle, is $3.4 \cdot 10^9$ ton/year. Roughly the same value by the order of magnitude is the continental discharge of calcium in the form of Ca^{2+} cations, somewhat higher than $0.5 \cdot 10^9$ ton/year. A slightly lesser amount is removed by streams in a suspended state, $0.471 \cdot 10^9$ tons per year. In addition, $0.048 \cdot 10^9$ tons of calcium per year is wind-blown off the land surface into the ocean.

The average calcium concentration in the oceanic atmospheric precipitation is 0.36 mg/liter, according to Savenko (1976). Therefore, the total of calcium, precipitated over the World's ocean during one year, is $164 \cdot 10^6$ tons; of this, the "dry" precipitation accounts for 20%, or $32.8 \cdot 10^6$ tons. The overall annual supply of calcium from ocean to the atmosphere is about $197 \cdot 10^6$ tons. About $22 \cdot 10^6$ tons is air-borne from ocean to land, and the rest is returned to the ocean. The average calcium concentration in atmospheric precipitation over land may be accepted as 3 mg/liter. The annual total of calcium, precipitated over the World's land surface, is $339 \cdot 10^6$ tons. With allowance made for 20% of "dry" precipitation ($68 \cdot 10^6$ tons), the overall calcium mass involved in the land-atmosphere cycle is $407 \cdot 10^6$ tons per year.

6.2. Global Potassium Cycle

Potassium, along with other alkaline and alkaline-earth elements, was accumulating in the Earth's crust during the melting stage. Most potassium became part of the crystalline matter at the late stages of magmatic crystallization. Potassium is a constituent of the most widespread silicates such as feldspar, amphibole, pyroxene, and mica. In the granitic layer of the crustal continental block, the average K_2O concentration is 2.89%, the mass of potassium being $198 \cdot 10^{15}$ tons. In the sedimentary shell, the average K_2O concentration is 1.87%, and the potassium mass, $38.2 \cdot 10^{15}$ tons.

In the hypergene metamorphosis of crystalline silicate structures, most potassium remains compositionally in newly-formed clay minerals and is merely in part released. Free potassium ions become involved in the aqueous migration and are also actively taken up by both disperse mineral matter and higher plants. For this reason, potassium is more tightly retained within the World's land confines as compared to calcium or sodium.

Potassium plays an important role in the life of both plants and animals. It takes part in photosynthesis and exerts influence on the carbohydrate,

nitrogen, and phosphorus metabolisms. In plants, potassium is stored in fruits and seeds and in the vegetative organs. The short supply of potassium in the soil results in a sharp drop of crop productivity. By virtue of its exceptional role, potassium is actively taken up by plants and is likewise actively engaged in the biological cycle. Its concentration in the living matter, 0.3%, is as high as that of nitrogen.

The average potassium concentration in the dry matter of terrestrial phytomass has been estimated from 0.7% (Bazilevich 1974) to 1.4% (Bowen 1966). In the marine algae, the potassium content is 5.2% by dry weight (Bowen 1966). Supposedly, the World's land vegetation, intact by man, contained about $25 \cdot 10^9$ tons of potassium, and the dry biomass of oceanic photosynthetic organisms, $0.176 \cdot 10^9$ tons. In the dead organic matter of the pedosphere, the average potassium concentration is close to 0.1-0.2%. Therefore, the potassium mass contained in the organic matter is several times less than that in the living matter and amounts to $3\text{-}6 \cdot 10^9$ tons.

Thus, some potassium released through weathering is taken up by the land vegetation to be partly stored in the dead organic matter. The main reserve of potassium in the pedosphere is provided for by a certain amount of potassium salts and by quite large masses of this element contained in clay minerals. However, a reliable estimate of these masses at present is difficult. Along with that the living matter of land and the finely-dispersed products of weathering retain a substantial part of potassium, another part of this element is involved in aqueous migration and is transported to the ocean, where $0.53 \cdot 10^{15}$ tons of potassium persists in a dissolved form. The sedimentary shell contains $38.2 \cdot 10^{15}$ tons of potassium.

To sum up the amount of potassium contained in the granitic layer, sedimentary shell, ocean, and other media of its occurrence, one obtains a value of $236.7\ 10^{15}$ tons. This value may be used to characterize the original potassium mass in the granitic layer of the lithosphere. An easy estimation will show that during the geological evolutionary buildup of the biosphere, some 16% of total potassium has been released from the granitic layer. However, the release of this element proceeded at a slower rate as compared to sodium, for which the respective value is 20%.

About $1.8 \cdot 10^9$ tons of potassium is involved in the biological cycle on land. In the ocean, the annual turnover of renewable mass of the photosynthetic organisms includes about $121 \cdot 10^7$ tons of potassium. The potassium mass released from the biological cycle on land is partly retained in the dead organic matter and taken up by pedosphere, and partly becomes involved in aqueous migration. Annually, the continental streams discharge into the ocean over $61 \cdot 10^6$ tons of free potassium ions. Still greater mass of this element is transported as dispersed suspended matter, mostly in the form of clay particles, about $283 \cdot 10^6$ ton/year.

Potassium, as a component of air-borne aerosols, actively migrates in a system "ocean surface-atmosphere-ocean surface". The average potassium concentration in the precipitation over the ocean is about 0.15 μg/liter. During one year, about $65 \cdot 10^6$ tons of potassium is precipitated with rain from atmosphere onto the ocean surface. Together with 20% of "dry" precipitation, this makes up to a total of $78 \cdot 10^6$ tons of potassium annually involved in the exchange between ocean and atmosphere. Of this, the land transport accounts for $0.005 \cdot 10^9$ tons, and about $0.06 \cdot 10^9$ tons is returned to the ocean.

The potassium ion concentration in continental rainfall is, on average, close to 0.7 μg/liter, totalling $0.05 \cdot 10^9$ tons. With allowance made for 20% of "dry" precipitation ($0.01 \cdot 10^9$ tons), about $0.068 \cdot 10^9$ tons of potassium ions is entrapped from land into the atmosphere, whereas a somewhat smaller amount, $0.065 \cdot 10^9$ tons, is precipitated because of the oceanic mass transport. An appreciable amount of potassium is carried over from land to ocean as dust. Having accepted the potassium concentration in dust to be the same as in clay deposits, the dust loss of the element is estimated as $0.043 \cdot 10^9$ tons.

6.3. Global Silicon Cycle

Silicon is the second (to oxygen) element in the crustal mass proportion. It was actively accumulated in the lithospheric matter at the melting stage. The concentration of this element in the upper mantle is about 19%, in basalts, 24%, and in granites, 32.3% (Vinogradov 1962). The silicon tetroxide tetrahedron, made up of a silicon cation tightly ligated to four oxygen anions, is a major structural unit of crystalline matter of the Earth's crust. In the granitic layer of the lithosphere, SiO_2 accounts for 63.08%, or $2427.5 \cdot 10^{15}$ tons of silicon.

The element of interest is ubiquitous in the natural waters and is widely used by vegetable and animal organisms in their building of the cell membranes, dense tissues, and skeleton. The average silicon concentration in terrestrial vegetation is 0.5% by dry weight, and in plankton, 5%, which corresponds to the respective masses of $12.5 \cdot 10^9$ and $0.17 \cdot 10^9$ tons. The biological cycle of the World's land and vegetation intact by man involved annually $0.86 \cdot 10^9$ tons.

The biological silicon cycle in the ocean is mainly provided for by the biotic activity of diatomaceous and radiolarian planktonic algae followed by the decay of their skeletons. The estimates of silicon mass involved in the biological cycle are at present rather discordant. One may presume, given an average concentration of 5% for silicon in plankton, that the biological turnover of silicon is $5.5 \cdot 10^9$ tons per year.

In the dead organic matter of land, the silicon concentration may tentatively be accepted as equal to 1%, the respective mass being $31 \cdot 10^9$ tons.

In natural waters, silicon occurs in the form of a neutral hydroxide $Si(OH)_4$ and, to a lesser extent, as anions of the $Si(OH)_3O^-$ type. Typical of its aqueous migration is the predominant transport from land to ocean, not counterbalanced by the reverse transport. The continental stream transportation accounts for $0.2 \cdot 10^9$ tons of soluble silicon compounds; in the ocean, their mass amounts to $4110 \cdot 10^9$ tons.

It is noteworthy that the elemental concentration in sea water is twice as low as that of stream water. One would hesitate to give an exact silicon concentration in the solid matter of continental run-off. Undoubtedly, it is higher over the concentration in argillaceous deposits, since a large amount of aleurite-arenaceous, mostly quartzitic, material is carried off the land. Given the average silicon concentration in the suspended stream matter, 117 μg/liter (Gordeyev 1983), the elemental mass transported as suspensions in streams is $4.8 \cdot 10^9$ tons per year.

Via transportation by wind, the land loses annually about $0.47 \cdot 10^9$ tons of silicon. Finally, along with the migration of a substantial amount of soluble silicon, the transport of this element in the form of clastic material is nearly 30 times higher. In the World's ocean, the soluble forms of silicon account for less than 0.001% of its mass in sedimentary rocks. According to Ronov (1976), the mass of sedimentary rocks contains 44.03% of SiO_2, which, in quantitative terms, corresponds to $493.6 \cdot 10^{15}$ tons Si. The total of silicon in the granitic layer and sedimentary shell amounts to $2\ 918 \cdot 10^{15}$ tons. Consequently, in the course of geological history, the Earth's crust has released about 17% of the total mass of silicon originally contained in the granitic layer of the lithosphere.

6.4. Global Phosphorus Cycle

Despite its low crustal abundance (about 0.1%), phosphorus plays a crucial role in the biosphere. Phosphorus originated as a melted-out component of the crustal matter. Its further evolutionary history in the lithosphere was complicated and in many details poorly understood. The phosphorus concentration in basalts is 0.14 and in granites twice as low, which makes its distribution similar to that of calcium. The phosphorus minerals are quite numerous (about 200 species) but, owing to the low crustal abundance of this element, they are not rock-forming ones. The overall phosphorus mass in the granitic block of lithosphere is $6.33 \cdot 10^{15}$ tons.

The important role of phosphorus in the biosphere is seen not in its high content, but in the fact that the protein synthesis is impossible in default of this element. The exothermal reaction of adenosine triphosphate with photo-

synthesized carbohydrates provides the subsequent biochemical reactions with energy. Along with carbon, oxygen, hydrogen, nitrogen, and sulfur, phosphorus is an element indispensable for the existence of living matter; simultaneously, it is a factor, not infrequently determinative of the biomass and productivity of living organisms. Many authors agree that the N-to-P ratio for the World's land vegetation lies within 10-15 (Basilevich 1974; Romankevich 1982; Bowen 1966), while other authors contend that this ratio is 2 (Zavarzin 1984). Anyway, almost in all natural biogeochemical systems, phosphorus is found in lesser amount than nitrogen, and precisely it is the former element that puts restriction on the mass of living matter. The effects arising from human activities change the N-to-P ratio to the benefit of phosphorus, which is conducive to ecologically unfavorable situations.

The average phosphorus concentration in the dry matter of terrestrial vegetation may be accepted as 0.2%; for the oceanic biomass, it is appreciably higher, 1.1% (Bowen 1966). In the terrestrial living matter undisturbed by man there was found about $5 \cdot 10^9$ tons of phosphorus, whereas in the oceanic biomass of photosynthetic organisms, it was $0.03\text{-}0.04 \cdot 10^9$ tons. A significant part of this element has been retained in the organic soil matter of the pedosphere, where the concentration of phosphorus is about 0.15%, the respective mass being $4.65 \cdot 10^9$ tons. The mass of phosphorus found in the mineral matter of soils at present defies exact determination.

An enormous amount of phosphorus is found in the World's ocean, where this element occurs in the form of solubilized anions, mostly PO_4^{3-}, HPO_4^{2-}, and also makes part of organic compounds. The turnover of this element because of its high need by the organism is quite significant and the organic-to-inorganic phosphorus ratio as well as the occurrence of phosphorus in living matter are subject to dynamic variation. For this reason the values characterizing the amount of various forms of this element in the ocean are rather arbitrary, although the sum total of it appears to be reliable enough. As a tentative estimate, one may accept that the C_0-to-P mass ratio in ocean is 100:1. The phosphorus concentrations in stream and sea water are fairly close to each other, being respectively 0.04 and 0.088 μg/liter.

Despite its low solubility, phosphorus is retained long in the ocean owing to the activity of living organisms striving to prevent the release of this element indispensable for their nutritional needs. Still, $1.311 \cdot 10^5$ tons of phosphorus is stored in the sedimentary rocks. The overall amount of phosphorus in the sedimentary shell and in the granitic layer of the crustal continental block is $6.33 \cdot 10^{15}$ tons. Therefore, slightly more than 17% of the total phosphorus mass, found in the granitic layer of the lithosphere, has been lost during the period of biosphere existence. The phosphorus distribution in the biosphere is as shown below.

Reservoirs:	Phosphorus mass, $1 \cdot 10^9$ tons
World's land	
Natural vegetation of land (intact by man)	5.0
Organic matter of pedosphere	4.7
Ocean	
Biomass of photosynthetic organisms	0.04
Soluble inorganic matter	15.0
Earth's crust	
Sedimentary shell	1 311 000
Granitic layer of continental block	6 330 000

Of major importance for the global phosphorus cycle are the elemental migrations in the closely related systems of the biological cycle and continental run-off. On land, $345 \cdot 10^6$ tons of phosphorus is annually involved in the biological cycle, and $1210 \cdot 10^6$ tons, in the biological cycle of photosynthetic organisms. The data as listed above show that phosphorus, similar to nitrogen, is more actively engaged in the biological cycle in the ocean, than on land. This attests to a limited availability of the two elements in the ocean, whereas on land, the living matter has a more nearly ample supply of them and can therefore afford their less intensive use.

The transport of phosphorus to the ocean is effected through the continental run-off. Phosphorus as supplied in streams makes part of the complex ions, dispersed organic matter, and mineral suspensions. Given the average concentration 0.04 μg/liter (*vide supra*), the annual supply of phosphorus in the ionic form to the ocean is about $1 \cdot 10^6$ tons. In the dispersed and partly solubilized organic matter, about 0.5% of phosphorus (by dry weight) is contained. This organic matter, on its transportation to the ocean, carries about $2 \cdot 10^6$ tons of phosphorus, which is 10 times as less than the transported amount of nitrogen in an analogous form. In spite of their relatively small masses, these forms exhibit a high reactivity and constitute a major reserve for use in the biological cycle.

The amount of phosphorus, transported as a suspended particulate material, is in a marked excess over the mass of soluble phosphorus forms. The average concentration of the suspended forms is 510 μg/liter (Gordeyev 1983), and the mass of element transported in suspension is estimated as $21 \cdot 10^6$ tons per year, which accounts for 88% of the total of stream-borne phosphorus. The off-

continental transportation by wind contributes but little to the balance. Phosphorus is tightly held in the air-borne particles, and only a small fraction of it can be released to be involved in the biological cycle.

The major mass fluxes contributing to the global phosphorus cycle are listed below ($1 \cdot 10^6$ ton/year):

World's land

Biological cycle (agricultural crops included)	345
stream loss	
(i) soluble inorganic compounds	1.0
(ii) dispersed organic matter	2.0
(iii) mineral suspension	21.0

Ocean

Biological cycle of photosynthetic organisms	1 210.0

The phosphorus mass lost into the sedimentary layer amounts roughly to $2\text{-}10 \cdot 10^6$ ton/year.

A characteristic feature of the global phosphorus cycle is the absence of a continuous geochemical transport of phosphorus back to land. The atmospheric transport of phosphorus as aerosol is of minor importance and cannot counterbalance the loss due to the continental run-off. The slow, but never-interrupted sedimentation in the ocean eliminates phosphorus from minor migration cycles. The global cycle for phosphorus is the most open one as compared to those of previously discussed elements. The only source of phosphorus supply to the global cycle is weatherworn continental rocks. The progressive loss of phosphorus from land can be offset only by the entrance into hypergenesis of the phosphorus-storing sedimentary rocks. Taking into account the long-term period for phosphorus removal from the ocean (tens of million years), one may presume that the performance of the global phosphorus cycle is provided for by tectonic processes translocating the phosphorus-rich sedimentary rocks into the zone of weathering.

Human activities affect substantially the phosphorus cycle within the World's land confines. The progressive agricultural application of phosphate fertilizers a significant part of which is subject to run-off losses constitutes one of the major factors in the eutrophization of lakes and the shallow coastal regions of epicontinental seas. About $14 \cdot 10^6$ tons of phosphorus per year is consumed in the production of phosphate fertilizers. No less extensive contamination by phosphorus compounds comes from domestic and industrial wastes. The data

as of 1985 have shown that the world-wide phosphorus losses from all sources was $12.15 \cdot 10^6$ ton/year (Evolution of Phosphorus Cycle... 1988).

The geochemical cycles of elements as discussed in this Section share a number of common features. First, all these cycles are maintained by the material supply from a single source, the lithosphere, or, more exact, from its granitic continental block. During the entire period of biosphere existence, 16.5% of potassium, 17% of both silicon and phosphorus, and 19% of sodium was released from the granitic crustal layer. Secondly, the major migratory masses are confined to the system of continental run-off and biological cycle. The atmospheric migration of elements is more restricted as compared to the migration of elements supplied to the geographic shell by mantle outgassing. For this reason, the elements of the latter group become actively accumulated in the World's ocean sediments. Most of the elements released from the granitic crustal block are found in the sedimentary rocks which contain over 99% of silicon, phosphorus, and calcium, about 98% of potassium and over 60% of sodium relative to the total of each of those elements in the biosphere. This makes the annual global cycles of phosphorus highly open, and a state of balance in phosphorus can be reached only on a long-term scale of a million and tens of million years.

Third, the living matter of the World's land, predominantly represented by terrestrial vegetation, contains a negligibly small part, some millionth fractions of the total mass of chemical elements, mobilized from the solid matter of continental crustal block by weathering. For these elements, like for those supplied to the biosphere through outgassing, the living matter serves not as a mass reservoir, but rather as a global biogeochemical separator.

Along with these common characteristics, each element exhibits its particular specificity, which becomes apparent in comparing the elemental mass distribution in biosphere (Table 6.1). An examination of the presented evidence will reveal that in the biomass, the most closely bound element is phosphorus, $38 \cdot 10^{-5}$% of its total, followed in decreasing order by calcium ($16.5 \cdot 10^{-5}$%), potassium ($6.5 \cdot 10^{-5}$%), sodium ($0.7 \cdot 10^{-5}$%), and silicon ($0.25 \cdot 10^{-5}$%). A comparison of the data in Tables 6.7 and 6.8 shows that, in the global biomass carbon, nitrogen, sulfur, phosphorus, calcium, and potassium are selectively retained. The presented evidence provides an idea of the relative importance of elements for the living matter of the World's land at its state of equilibrium with the environment. It should be noted that equally essential in this process are all intervening elements, those outgassed and those released from the granitic layer.

The relative mass distribution of the above elements in the World's ocean is also different. Contained in the ocean are over 35% of sodium, slightly more than 2% of potassium, about 0.01% of phosphorus, and less than 0.001% of silicon. Irrespective of this, more calcium is involved in the biological cycle on land, and more phosphorus and sodium, in the ocean. A minimal difference

Table 6.1. Mass Distribution of Chemical Elements as Supplied to Biosphere from the Granitic Layer of the Continental Crust

Reservoir	Element and mass of, $1 \cdot 10^6$ tons				
	P	K	Ca	Na	Si
World's land:					
vegetation	5.0	25.0	45.0	3.0	12.5
	(38)	(6.5)	(16.5)	(0.7)	(0.25)
organic matter of pedosphere	4.7	6.0	15.0	0.3	31.0
	(36)	(1.5)	(5.5)	(0.07)	(0.6)
Ocean:					
photosynthetic organisms	0.04	0.17	0.034	0.09	0.17
	(0.3)	(0.04)	(0.01)	(0.02)	(0.01)
soluble organic matter	30.0	nil	nil	nil	nil
	(229)				
solubilized inorganic ions	120.0	530000	559000	14740000	4100
Sedimentary shell	$1.311 \cdot 10^6$	$38.2 \cdot 10^6$	$272.8 \cdot 10^6$	$26.7 \cdot 10^6$	$493.6 \cdot 10^6$
Element mass in biosphere, $1 \cdot 10^{15}$ tons	1.3	38.7	273.4	41.4	493.6

Figures in parentheses indicate $1 \cdot 10^{-5}$% of the total element mass in biosphere

is observed between the involvement of potassium and silicon in the biological cycle of continents and oceans. The elements whose occurrence in the ocean is larger than 0.1% of their mass in the biosphere take an active part in the ocean vs. atmosphere mass exchange and migrate from ocean onto land to counterbalance in part the continental run-off loss. Such elements are sodium, with 35% of its mass found in the ocean, and calcium (2%). These elements, as well as the outgassed sulfur (11%) and chlorine (80%) have been classified as cyclic ones implying thereby their substantial involvement in the migration cycles within a system "land-ocean-atmosphere-land".

6.5. Global Cycles for Heavy Metals

Heavy metals play a special role in the biosphere. They mostly occur in a dispersed state, but are also capable of forming local accumulations where their concentrations are hundreds and thousands times higher than their crustal abundances. Metals make no part of the organic compounds constitutive of the tissues of living organisms. At the same time, the electronic structure of heavy metals imparts to them a property of variable valence which makes possible the interaction of metals with nitrogen- and sulfur-containing functional groups of organic compounds.

In this capacity, the metals become an essential part of the enzymatic system of living organisms as a functional basis of the living matter of the Earth. On the other hand, the metals, being one of the major natural resources for use by the world economy, constitute a group of hazardous environmental contaminants. The elucidation of global processes in metal biogeochemistry is now seen as a very urgent problem.

The biogeochemical cycles of heavy metals have much in common. By way of example, let us consider the distribution and migration in the biosphere of lead and zinc as typical representatives of the group of heavy metals.

6.6. Global Lead Cycle

The Earth's crust becomes increasingly high in lead on passing from the upper mantle to the granitic layer where the lead concentration is 16 μg/g. The accumulation of lead in the Earth's crust proceeded via its melting out from the mantle matter, simultaneously with the formation of radiogenic isotopes ^{206}Pb, ^{207}Pb, and ^{208}Pb. The ^{204}Pb isotope has no radioactive precursors. Its concentration has remained unchanged since the earliest stage of geogenesis, whereas the concentrations of radiogenic isotopes tended to gradually increase. Presumably, about 1/3 of the crustal lead has originated from the isotopic decay of uranium ^{238}U and ^{235}U and thorium ^{232}Th.

The lead concentration in the Earth's crust and even in closely related rocks is widely varied; commonly, the lead distribution is approximated by a lognormal curve. Lead, along with its habitual occurrence in a dispersed state, also forms diverse natural accumulations in which its concentration is thousands of times higher than its crustal abundance.

The rock weathering leads to the release of Pb^{2+} ions from the decayed structures of crystalline rock-forming minerals. Most of the released ions are taken up by finely-dispersed clay particles and iron hydroxide gels. A small part of liberated lead is supplied in the form of simple and complex ions to

surface and underground waters. The average concentration of soluble lead compounds in the continental run-off is close to 1 μg/liter, and that of lead-containing suspensions, to 100 μg/liter. The stream loss of water-soluble lead is about $41 \cdot 10^3$ ton/year, and of lead in suspension, $4100 \cdot 10^3$ ton/year. The finely-dispersed organic detritus as a component of stream suspensions transports about $10 \cdot 10^3$ tons of lead per year. About the same amount of lead migrates as components of water-soluble compounds. Over 90% of suspensions and a substantial percentage of water-soluble compounds become deposited in the deltas, estuaries, and the narrow strip of coastal shelf. The pelagic part of the ocean receives no more than $200 \cdot 10^3$ ton/year of lead in suspension and $25\text{-}30 \cdot 10^3$ ton/year of soluble lead compounds. Further, owing to the biofiltration of sea water by plankton organisms, a significant part of suspensions and a certain part of water-soluble compounds are deposited as precipitates. This process is differentiated, and among the trace metals lead is the most active to precipitate.

The average lead concentration in the ocean is 0.03 μg/liter, the overall mass being $41 \cdot 10^6$ tons. The time required for a complete turnover of this mass at the expense of stream transport (with no account of the deposition of soluble lead in the deltas and estuaries) has been estimated as one thousand years; the said deposition having been taken into account (30-40%), the turnover period extends to 1.5-1.9 thousand years. The lead concentration in suspensions is about 1 μg/liter, and the respective metal mass is $0.014 \cdot 10^6$ tons. In the sedimentary shell, $35\text{-}40 \cdot 10^{12}$ tons of lead is stored, whereas the granitic layer of the crustal continental block contains $131 \cdot 10^{12}$ tons. Thus, the biosphere accounts for 23.5% and the granitic layer for 76.5% of the sum total of lead content.

A significant amount of lead is supplied to the ocean from hydrothermal sources some of which are quite high in lead. As an example, one may refer to the metalliferous chloride solutions in deep-sea rift depressions in the Red Sea. According to the data by Lisitsin (1983), in the Pacific, the supply of lead from hydrothermal sources is more than 10% of the soluble lead transported in streams.

The available data on lead concentration in photosynthetic organisms are contradictory. The average concentration appears to be close to 1 μg/g of dry biomass. If this is correct, the biomass of oceanic photosynthetic organisms must contain $0.004 \cdot 10^6$ tons of lead, and the annual lead turnover involving these organisms must be $0.11 \cdot 10^6$ tons.

The average lead concentration in terrestrial vegetation is 1.25 μg/g by dry weight. In the vegetable biomass of the World's land, free from human activities, there was contained $3.1 \cdot 10^6$ tons, and the biological turnover involved $0.21 \cdot 10^6$ tons of lead per year. Noteworthy, the uptake of lead by terrestrial vegetation is less intense than that of zinc, copper, and some other metals. The overall coefficient of biological absorption K_b, defined as the ratio of the

average metal concentration in terrestrial vegetation ash to the metal abundance in crustal granitic layer is 1.5.

Lead, along with its delivery through the root system, can be supplied to the plants from precipitation via its uptake by the leaf laminas. Simultaneously, the green parts of plants exude lead as a component of phytoncides and nonvolatile compounds which are either carried away with the wind, or washed down by the rain. The lead content in the condensate of coniferous trees of subalpean forests in certain ore-bearing regions of the USA has been found to be 1 to 12 μg/g, in contrast to its much smaller content in ore-free regions (Curtin *et al.* 1974).

According to Beaufort *et al.* (1975), the vegetation can produce during one year 5 g of lead per square kilometer. This is a way to supply 250-300 tons of metal per year to the lowest tropospheric layer. Besides, significant amounts of lead, considering its large accumulations in the phytomass of forest biocenoses, find their way to the troposphere during forest wildfires.

The lead concentration in the organic matter of pedosphere is close to 2–3 μg/g, the metal mass being $9\,10^6$ tons. The lead distribution in the biosphere is as shown below.

Reservoirs:	**Mass, tons of Pb**
World's land	
troposphere	$0.003 \cdot 10^6$
continental vegetation	$3.1 \cdot 10^6$
organic matter of pedosphere	$9.0 \cdot 10^6$
Ocean	
troposphere	$0.001.10^6$
photosynthetic organisms	$0.004 \cdot 10^6$
soluble salt ions	$41 \cdot 10^6$
suspensions	$0.14 \cdot 10^6$
Earth's crust	
sedimentary shell	$32 \cdot 10^{12}$
granitic layer	$131.2 \cdot 10^{12}$

The lead concentration in the troposphere over the continents varies from 0.2-0.5 ng/m^3 to 300-400 ng/m^3 for nonurbanized regions. Such a wide range is due to a variety of natural factors of which the most important appears to be the finely-dispersed mineral dust. At a minimum dust level, the air-borne lead concentration varies within a narrower range of 0.5 to 8 ng/m^3 (Zhigalovskaya *et al.* 1974; Chow *et al.* 1970). The lowest lead concentration has been recorded in the Antarctic air where the snow precipitation removes completely from the troposphere the negligible amounts of continental dust.

In friable products of weathering that make part of the continental cover and are exposed to the wind, the lead concentration is $20 \cdot 10^{-4}$%. Given the average dust concentration in the troposphere, about 30 μg/m^3 one should expect to find 0.6 ng of lead in 1 m^3 of air and, accordingly, 0.6 g in 1 km^3. In reality, the metal concentration in continental aerosols is, as a rule, appreciably higher ranging from 30-50 μg/g to 100-500 μg/g. The increase in concentration is due to the uptake by the aerosol particles of dispersed lead as supplied from other sources. The coefficient of aerosol accumulation K_a for lead, defined as the ratio of the lead concentration in solid aerosol phase to the lead abundance in crustal granitic layer falls commonly into a range of 30-60. The above aerosol lead concentrations provide for the lead content, respectively, from 0.9-1.5 to 3-15 ng per square meter. At such concentrations, one is expected to find 1-15 g of lead per 1 km^3 in the lowermost tropospheric layer. Thus, the difference between the lead concentration in the weatherworn products and the lead concentration in the solid aerosol phase appears to be quite significant. This difference turns out to become even greater with the allowance made for the cyclic dust migration in the troposphere.

For most of the lead-carrying dust particles, the period of complete renewal ("aerosol life-time") is commonly about 7 days. Consequently, it may be presumed that the cyclic turnover of dust particles within the system "land surface-troposphere" is about 50 per year. The overall aerosol precipitation supplies to the land surface $10 \cdot 10^3$ to $75 \cdot 10^3$ tons of metal per year, or an average of $50 \cdot 10^3$ ton/year. Along with this, $40\text{-}50 \cdot 10^3$ tons of tropospheric dust-borne metal is precipitated over the World's ocean.

By the action of continuous condensation and evaporation of water, the dust particles accumulate soluble metal forms which are finally washed out by rainfall. The average lead concentration in the precipitation over noncontaminated territories may be accepted as equal to 1 μg/liter, although in many nonurbanized regions it reaches 2-4 μg/liter, or even higher (Zhigalovskaya *et al.* 1974; Chow *et al.* 1970). The supply of soluble lead forms to the World's land by precipitation may be estimated as $n \cdot 110 \cdot 10^3$ ton/year, with n changing from 1 to 3 according to the concentration range of 1 to 3 μg/liter. This value includes also about $n \cdot 40 \cdot 10^3$ ton/year for the lead transported to land via precipitation of oceanic origin.

In comparing the lead masses (those supplied to the troposphere as continental dust and those precipitated in the liquid and solid state over the land) one will perceive an apparent imbalance: the tropospheric lead precipitation is larger than the lead mass blown away by the wind from the weatherworn land surface. A similar situation appears to occur within the system "World's ocean-troposphere", where the atmospheric precipitation of lead is much higher than the lead mass supplied to the troposphere as sea water salts carried over by the wind.

According to the available evidence (Bezborodov *et al.* 1984; Chester *et al.* 1974), the average lead concentration in oceanic aerosols may be accepted as 230 μg/g. This is higher by an order of magnitude over the metal concentration in the weatherworn land surface, and much higher over that in sea water. The average concentration of air-borne lead over the ocean is about 3 ng/m^3 (Bezborodov *et al.* 1983). Apparently, processes are operative contributing to the enrichment of oceanic aerosols with lead and other heavy metals. The estimate of metal mass, precipitated from the troposphere, is suggestive of such a possibility. The lead concentration in rainfall water being 1 to 6 μg/liter, the supply of lead to ocean by liquid atmospheric precipitation is estimated as $400 \cdot 10^3$ to $2500 \cdot 10^3$ tons per year. The dry precipitation apparently provides about $50 \cdot 10^3$ (within a range of $20 \cdot 10^3$ to $100 \cdot 10^3$) tons of lead per year. Thus, the overall delivery of lead from troposphere to the ocean amounts to a total of hundreds of thousand, or even a few million tons, which is in great excess over the lead supply to the atmosphere via continental dust and sea salts. Consequently, there must be other sources of metal supply to troposphere.

The selective enrichment of aerosols in lead and other metals is due to a number of factors, of which the most important is biometallization, that is, the production of tetramethyl lead by microorganisms (Craig 1980). The volcanic emanations and the sorption of metals by the water films of gas bubbles also contribute in a certain measure to the enrichment of the atmosphere in lead.

The presented evidence allows us to outline the dynamics of lead mass exchange in the biosphere in the following manner. The metal masses occur in a state of dispersal, and their migration displays a clearly cyclic character. Apart from the living matter, the dispersed lead migrates either as a soluble form, or as a solid-phase constituent. The major source of solid lead forms are the pedosphere and unconsolidated products of weathering. The transportation of these forms to the ocean is mostly effected through river streams ($4100 \cdot 10^3$ ton/year), and partly through the atmosphere (about $40 \cdot 10^3$ ton/year). In the continental mass-exchange with the atmosphere, 100 to $300 \cdot 10^3$ ton/year of solid-phase lead is involved, including about $30 \cdot 10^3$ ton/year from volcanic ash discharge. At least $350 \cdot 10^3$ tons of solid-state lead is annually supplied to the continents as domestic and industrial wastes.

The World's ocean is a global accumulator of soluble lead forms. Owing to the selective release of lead at the ocean-troposphere interface, $500\text{-}2300 \cdot 10^3$ tons per year of soluble forms of this metal is supplied to the troposphere. Almost all this mass is retained within the ocean-troposphere cycle, and merely $n \cdot 40 \cdot 10^3$ tons per year (n = 1 to 3) is transported to the continents by air masses of oceanic origin. The stream loss of soluble lead forms from the continents is about $40 \cdot 10^3$ ton/year, to which is added at least $20 \cdot 10^3$ tons per year of soluble lead compounds of anthropogenic origin. $100\text{-}300 \cdot 10^3$ ton/year of soluble

lead forms is precipitated from the troposphere onto the continents, including $40\text{-}120 \cdot 10^3$ tons per year of air-borne masses of oceanic origin. About $2 \cdot 10^3$ ton/year is supplied by volcanic gases, and some $10 \cdot 10^3$ ton/year, by the emanations from vegetation. Added to the troposphere is also $4\text{-}8 \cdot 10^3$ tons per year of soluble anthropogenic forms. Apparently, during the tropospheric migration, part of the solid-state lead becomes transformed into a soluble state. For this reason, both the surficial layers of pedosphere and the vegetative cover receive soluble lead forms in substantial excess over those involved in the mass exchange with the atmosphere.

The living matter takes up the dispersed lead from solutions and partly from the solid phase and entrains it in biological migration at a rate of $210 \cdot 10^3$ ton/year on land, and at least $110 \cdot 10^3$ ton/year in the ocean.

The proportion of various forms of lead in the migratory fluxes is controlled by global mechanisms such as oceanogenic sedimentation, fractionation at the ocean-troposphere interface, aerosol formation, also processes occurring in the pedosphere. In the global migration cycle of lead, a quite important role is assigned to the pedosphere. In soils, the redistribution of various forms of lead takes place via interdependent equilibria. Large masses of soluble lead as supplied to the land surface through cyclic migration become taken up by dispersed particles to make part of sparingly soluble compounds. The elevated lead concentration in the upper soil horizon was traditionally explained as due to the accumulative activity of plants. Recent findings have suggested that this effect is to a certain extent associated with the cyclic lead migration within the "land surface-troposphere" system.

6.7. Global Zinc Cycle

The geochemistry of zinc and lead in the Earth's crust are closely related. The zinc concentration, similar to lead concentration, tends to increase on passing from the upper mantle ($3 \cdot 10^{-3}$%) toward the basaltic ($1.3 \cdot 10^{-2}$%) and further on to the granitic layer ($6 \cdot 10^{-2}$%). Substantial masses of zinc and lead are found in the postmagmatic formations. The zinc-lead ore deposits (the so-called complex ore deposits) have accumulated over $20 \cdot 10^6$ tons of zinc. This enormous quantity accounts for a mere 0.001% of the zinc mass occurring in a dispersed state in the uppermost granitic crustal layer 1 km deep.

The biospheric geochemistries of zinc and lead differ appreciably. This stems from the substantially different roles of the two elements in the performance of the terrestrial living matter. Lead, viewed from a physiological standpoint, is an element of minor importance and in this respect differs little from other dispersed metals which are taken up by terrestrial plants. By contrast, zinc is

one of the essential trace elements, it is a constituent part of enzymes which control numerous biotic processes. It takes part in the synthesis of ribonucleic acids and chlorophill. Zinc-containing enzymes are involved in the carbohydrate and phosphate metabolisms. The Zn-enzyme carboanhydrase, present in the erythrocytes, is very important for the physiology of animal organisms. Zinc plays a very essential role in the gonadal activity of animals and is involved in the mechanisms providing for the resistance of plants to frost and drought (Kabata-Pendias *et al.* 1989). Zinc is actively taken up by the World's land vegetation. The global coefficient of biological absorption (K_b), defined as the ratio of the average concentration of a metal in the annual production of terrestrial vegetation to the metal abundance in the granitic crustal layer, is 12 for zinc, whereas for lead, it is slightly higher than 1.

The zinc concentration in terrestrial plants is widely varied depending on the pedo-geochemical conditions. Plants are known that grow on territories with abnormally high zinc concentration in the soil and whose zinc content reaches 10 or even 17% by dry ash weight (the so-called galmei floras). At the same time, the available wealth of data provide evidence for a relatively small concentrational zinc variation in definite systematic groups of plants. In the widespread representatives of natural flora of the USA, the zinc concentration falls within a range of 320-640 μg/g by ash weight (Connor and Shacklette 1975; Ebens and Shacklette 1982), whereas for the most typical plant vegetation of the South Urals (Russia), it is 150-750 μg/g by ash weight. According to Brooks (1983), the average zinc concentration in plants is 50 μg/g on a dry weight basis, that is, about 1000 μg/g by ash weight. We believe, according to our estimates, that the average zinc concentration in the annual production of the World's land vegetation may be accepted as equal to 600 μg/g by ash weight, which corresponds to 30 μg/g for dry phytomass, or 12 μg/g for live weight of plants. On the basis of this estimate, the overall biomass of land vegetation, contributed by man, might have contained about $75 \cdot 10^6$ tons of zinc, the annual growth uptake of the metal being $5.2 \cdot 10^6$ ton/year. About the same amount of zinc was returned to the pedosphere.

Most zinc in plants is confined to easily degradable tissues and is therefore promptly removed from the plant remains as distinct from lead which is tightly held in plant remains. The average zinc concentration in peat and forest litter is about 20 μg/g by dry weight and in humus, 4-5 times higher. Accordingly, the metal content in peat and forest litter is $14 \cdot 10^6$ tons. It may be presumed therefore that the organic matter of the pedosphere contains about $200 \cdot 10^6$ tons of zinc.

The overall content of all zinc forms in the humic horizon of the soils in Russia varies from 20 to 80 μg/g. The average zinc concentration in the humic layer of the soils in the European part of the Russian territory is about 50 μg/g. Close in value is the geometric mean for zinc concentration in the

soils of the USA, 48 μg/g (Shacklette *et al.* 1984). Fifty to sixty percent of the total zinc in soil is complexed to the organic matter and sorbed on the iron hydroxide films. The percentage of tightly held zinc in soils is much higher (up to 80-90%).

The water-soluble zinc species account for a very small fraction of the total of metal in the soil, and are actively involved in the aqueous migration. The global coefficient of aqueous migration (K_a) for zinc is greater than 3, whereas for lead, it is 0.5. The average zinc concentration in the world streams is about 20 μg/liter, and the mass of zinc transported therein is $820 \cdot 10^3$ tons per year. The average zinc concentration in stream suspension is much higher, 143 μg/liter (Gordeyev 1983), and the respective transported mass is $5.8 \cdot 10^6$ tons per year. Thus, the mass transport of suspended zinc accounts for 87% of the total stream loss of zinc; for comparison, the respective value for lead in suspension is greater than 98%.

Zinc takes an active part in the mass exchange between the World's land and troposphere. According to Beaufort *et al.* (1975), an area of 1 m^2 of tree leaves can annually exude up to 9 kg of Zn as a terpene component. A significant quantity of volatile organozinc compounds is released by plants under the conditions typical of sea coasts and subaquatic landscapes owing to bacterial biometallization. Regrettably, the involvement of zinc in those processes is as yet difficult to quantify.

In the surficial air layer over a territory free of technogenic interference, the zinc concentration is 2 to 70 ng/m^3 (Ostromogil'sky *et al.* 1981). Consequently, over an area of 1 km^2 in a layer 1 km high, is found 2 to 70 g of zinc, and over the entire World's land, except for the glaciated areas and those occupied by internal water bodies, the respective layer contains 270 to 9450 tons, or 500-5000 tons of zinc on the average.

A certain amount of zinc is supplied to the atmosphere in mineral dust. The average zinc concentration in the soft covering deposits exposed to deflation is 50 μg/g. Carried over to the troposphere in dust is $250\text{-}300 \cdot 10^3$ tons of Zn per year, of which about $90 \cdot 10^3$ tons is transported to the ocean, and $160\text{-}210 \cdot 10^3$ tons is precipitated over the land surface.

The natural zinc concentrations in the precipitation over various territories differ markedly. The smallest concentrations are typical of polar and high mountain regions whose air contains little dust. In the antarctic snow, the zinc concentration is a few hundredths of a microgram per liter, in the snow of Greenland, it is higher by an order of magnitude (Burton 1978; Herron *et al.* 1977). In the snow cover of Spitzbergen, the zinc concentration reaches 31 μg/liter (Evseyev 1988). In the snow precipitated in mountainous regions of Central Eurasia, the measured zinc concentration was a few tens of micrograms per liter (Kulmatov 1988).

The rainfall zinc concentration for land territories free of direct technogenic contamination is 10-40 μg/liter; in reality, the concentration at particular

localities may exceed the indicated limits. Given the average concentration of 20 μg/liter, one comes to an estimate of $2.28 \cdot 10^6$ tons of Zn per year precipitated from the atmosphere onto the World's land surface. Thus the atmospheric precipitation supplies to land surface much more soluble zinc compounds as compared to those blown away into the atmosphere as mineral dust. A plausible explanation of the fact is that emitted to the atmosphere are also gaseous zinc compounds which are taken up by aerosols to be later washed out by rainfall. For this reason, the zinc concentration in solid aerosols sampled in the lowermost air layer is 10-30 times higher than the crustal zinc abundance.

The gaseous zinc compounds are supplied to the atmosphere during volcanic eruptions and through release of volatile organic compounds by green plants and bacteria. The volcanic emission of zinc is about $216 \cdot 10^3$ ton/year. Of this, about $150 \cdot 10^3$ tons becomes entrapped by air-borne dispersed particles of 0.001-0.05 mm in size and may be washed out by rainfall. The data presented indicate that the zinc mass of volcanic origin is appreciably smaller than that supplied through atmospheric precipitation. Apparently, the major source of atmospheric zinc is the above-mentioned bacterial biometallization.

Important information is provided by the data on zinc distribution in the Earth's crust.

The average zinc concentration in the main groups of sedimentary rocks is (in μg/g): clay and argillaceous slate, 95; sandstone, 16; carbonate rock, 20 (Turekian *et al.* 1961). Accordingly, the respective zinc mass is: clay and argillaceous slate, $108 \cdot 10^{12}$ tons; sandstone, $6.9 \cdot 10^{12}$ tons; carbonate rock, $14.2 \cdot 10^{112}$ tons. The overall zinc mass in the sedimentary shell is $129.1 \cdot 10^{12}$ tons. The zinc mass in the granitic layer of the crustal continental block is $419 \cdot 10^{12}$ tons. The total zinc mass in the granitic layer and sedimentary shell is $547 \cdot 10^{12}$ tons. Thus, during the entire period of geological history, over 23% of the total zinc mass has been deposited in the sedimentary shell. This value is in excess of the percentage of elemental mass release (17-19%) by hypergene metamorphosis of the granitic layer. Presumably, a certain additional quantity of zinc has been supplied to the biosphere owing to outgassing processes.

Most of the zinc in the ocean is represented by water-soluble inorganic compounds. According to the data of Lisitsin *et al.* (1983), 90% of zinc suspended in the river stream, and 35% of soluble zinc are deposited at the ocean-land interface. As a result, the pelagic part of the ocean receives annually about $0.6 \cdot 10^6$ tons of zinc in suspension and less than $0.5 \cdot 10^6$ tons of soluble zinc. The average concentration of soluble zinc in the ocean is close to 5 μg/liter, the respective mass being $6.8 \cdot 10^9$ tons. The mass of zinc found in the ocean in a suspended state is much smaller and is as yet difficult to assess quantitatively.

The zinc concentration in oceanic photosynthetic organisms as well as in terrestrial ones varies within 38-850 μg/g by dry weight or even higher (Demina *et al.* 1983; Bryan 1976). Starting from an average concentration of 50 μg/g, the

amount of zinc in the biomass of oceanic photosynthetic organisms is estimated as $170 \cdot 10^3$ tons. This is very small as compared to the mass of zinc contained in the World's land vegetation. Simultaneously, very short life cycles of plankton organisms provide for a high rate of the biomass renewal and for a high biological productivity of the ocean. During one year, about $30 \cdot 10^6$ tons of zinc becomes assimilated by the oceanic photosynthetic organisms, which is several times higher than the annual uptake of zinc by land vegetation. Certainly, it should be kept in mind that owing to the high turnover rate of the plankton, the annual uptake is in fact estimated through multiple summation of the same zinc mass involved in the complete cycling of plankton biomass.

There have been reports (Demina *et al.* 1983) that, owing to the active use of zinc by plankton organisms, 4 to 50% of soluble zinc in different regions of the ocean is accounted for by metabolites, complex organometal compounds.

Balance estimates have shown that the oceanic troposphere contains more heavy metals than one might have expected as derived from the sea water entrainment by wind. The zinc concentration in the lowermost troposphere layer ranges widely from a few hundredths of a nanogram to 60 nanograms per cube meter. According to the data by Bezborodov *et al.* (1984), the average zinc concentration over the pelagic regions of the ocean is 7.8 ng/m^3. Consequently, $2.8 \cdot 10^3$ tons of zinc is found in the lowermost troposphere layer 1 km high over the World's ocean. The average zinc concentration in rainfall over the pelagic part of the ocean is close to 6 μg/liter (Bezborodov *et al.* 1984). The atmospheric precipitation of soluble zinc over the ocean surface is about $2.5 \cdot 10^6$ ton/year. This is in a three-fold excess over the supply of soluble zinc via global run-off.

One may presume that the major source for the zinc supply to the troposphere over the ocean is the microbiological metal methylation (Craig 1980; Wood 1974). Besides, about $1 \cdot 10^6$ tons of dust-borne zinc per year is carried over to the oceanic troposphere from the continents. In turn, $260 \cdot 10^3$ tons of air-borne Zn per year is transported from the oceanic troposphere to be precipitated to land.

Based on the above evidence, the zinc distribution in biosphere is seen in the following manner.

Reservoir	Mass, tons of Zn
World's land	
Lower troposphere	$0.0005\text{-}0.005 \cdot 10^6$
Continental vegetation	$75 \cdot 10^6$
Pedosphere	
Peat and forest litter	$14 \cdot 10^6$

Ocean	
Lower troposphere	$0.0028 \cdot 10^6$
Photosynthetic organisms	$0.17 \cdot 10^6$
Soluble forms	$6800 \cdot 10^6$
Earth's crust	
Sedimentary shell	$134 \cdot 10^{12}$
Granitic layer	$490 \cdot 10^{12}$

6.8. General Characterization of Cycles and Metal Distribution

As follows from the foregoing evidence, the biospheric geochemistry of lead and zinc displays a number of common features. First, over 99.9% of the mass of these metals occurring in the biosphere is confined to the sedimentary shell. Secondly, in the global mass exchange of lead and zinc, of prime importance are the processes that are carried out on the World's land with the assistance of living organisms: (i) the cycling of chemical elements associated with the photosynthesis and the subsequent degradation of organic matter; (ii) mobilization of the elements from rocks during the pedogenesis and their involvement in the aqueous migration; (iii) release into the troposphere of gaseous metabolites from higher plants and microorganisms. Similar processes are typical of the migration cycles of other representatives of the heavy metal group and their multivalent congeners (arsenic, bismuth, antimony).

The heavy metals were released into the aqueous and gaseous shells of the Earth at the earliest formative stage. The proportion of gaseous and water-soluble forms of metals was controlled by the respective physico-chemical equilibria, and the excess masses were deposited as precipitates. At later stages, the biogeochemical activity of living organisms became an essential factor in these processes, which has resulted in the structural transformation of primary abiogenesis into a system of biogeochemical cycles interrelated through mass exchange. The sedimentary shell was continuously performing the function of a colossal geochemical repository for storing excess metal masses. From this repository, the metals returned to the migration cycles only when the sedimentary layers, by virtue of tectonic phenomena, emerged to the World's land surface to become exposed to biogeochemical factors.

One is faced with a problem in attempting to define the sources for supply of heavy metals to the aqueous and gaseous media. It is to be recalled that the quantity of a chemical element as entered into the migration cycling via mobilization from the upper part of the continental Earth's crust (the so-called granitic layer) and later deposited in the sedimentary shell accounts for

Table 6.2. Heavy Metal Mass Distribution in Sedimentary Shell

Metal	Metal mass, $1 \cdot 10^{12}$ tons, in:				% of total mass of sedimentary shell plus granitic layer
	main groups of sedimentary rocks			sedimentary shell	
	argillaceous	carbonate	sandy		
Fe	53808	2698	4214	60720	17.1
Mn	969	781	2.1	1752	23.4
V	148.2	14.2	8.6	171	21.5
Cr	102.6	24.8	4.7	132.2	32.1
Zn	108.3	14.2	6.9	129.4	23.6
Cu	51.3	2.84	2.15	56.3	23.8
Pb	22.8	6.39	3.01	32.2	19.8
Ni	77.5	14.2	0.86	92.5	30.2
Co	21.66	0.071	0.129	21.86	26.6
Mo	2.96	0.284	0.086	3.32	32.2
Cd	0.34	0.025	0.021	0.39	22.9
Hg	0.57	0.028	0.013	0.61	70.1

17-20% of the initial element amount. Considering that over 99.9% of each of the heavy metals that have been supplied to the biosphere during the geological history is found in the sedimentary shell, the original metal quantity is practically equal to the sum of metal masses contained in the granitic layer and in the sedimentary shell.

For a solution of this problem, of importance is the possibly more exact determination of metal masses in the sedimentary shell. Summarized in Table 6.2 are the metal masses as determined by the average mass concentrations in the main groups of sedimentary deposits (clay and argillaceous slate, carbonate rock, sand and sandstone) after Turekian *et al.* (1961) and Ronov *et al.* (1976). One will observe in Table 6.2 that the relative content (%) of trace heavy metals in the sedimentary shell is higher than the relative content (%) of iron as supplied to the biosphere through weathering only. The mass of a trace element is, as a rule, higher than the 20% of its sum total mass for sedimentary shell and granitic layer. This fact provides a good reason to presume that the metals have been supplied to the biosphere not only through their mobilization due to rock weathering, but also in part through outgassing. It stands to reason that mercury as the most volatile metal was the most susceptible one to outgassing; the mass of this metal in the sedimentary shell is in excess of its mass in the granitic layer and accounts for more than 70% of the sum total for sedimentary shell and granitic continental layer.

Table 6.3. Mass Distribution of Heavy Metals in Biosphere

Metal	Metal mass in:			
	World's land vegetation, $1 \cdot 10^6$ tons	ocean (soluble forms) $1 \cdot 10^6$ tons	sedimentary shell, $1 \cdot 10^{12}$ tons	granitic layer of continental crust, $1 \cdot 10^{12}$ tons
Fe	500.0	4658	60720	259200
Mn	600.0	548	1752	5740
V	3.75		171	623
Cr	4.50	274	132	278
Zn	75	6850	129	418
Cu	20	1233	56	180
Pb	3.13	41.1	32	131
Ni	5	685	92	213
Co	1.3	41.1	22	60
Mo	1.2		3.3	11
Cd	0.09	151	0.4	1.3
Hg	0.03	206	0.6	0.26

The available evidence permits reaching a conclusion that during the entire period of geological history, the natural waters were saturated with heavy metals which, once in excess, deposited precipitates. For this reason, the living organisms could exist and develop under the conditions of natural waters saturated with metals whose concentration was maintained at an acceptable level owing to the equilibria within a water-precipitate system.

Most of dissolved metals are found in the ocean water, and their lesser part, in the planetary living matter (mainly as components of the World's land vegetation) and in the organic matter of the pedosphere. The available data on metals bound to the soluble organic matter of ocean are as yet too scarce to allow a quantitative estimation. It may merely be presumed that the soluble organic matter contains more metals than the biomass of all oceanic organisms. The heavy metal distribution in the biosphere is summarized in Table 6.3. For comparison, Table 6.3 lists also the metal masses contained in the granitic continental layer of the Earth's crust.

The global mass exchange of heavy metals remains as yet unclear in many details. For this reason, the data presented in Table 6.4 refer only to the major well-studied migratory mass fluxes on the World's land surface. For comparison data are also given on the biological metal cycle involving the activity of photosynthetic oceanic organisms. The average metal concentrations in phytoplankton as reported by Bryan (1976) have been used in calculations.

Table 6.4. Migratory Fluxes of Heavy Metals on the World's Land Surface

Metals	Metal mass turnover, $1 \cdot 10^6$ ton/year					
	biological cycle on World's land	stream loss		dust-borne loss from continents	transport from ocean to land	biological cycle of oceanic photosynthetic organisms
		in solution	in suspension			
Fe	34.0	27.47	963.0	65.0	0.132	47.3
Mn	41.0	0.410	20.5	4.0	0.176	0.99
Zn	5.20	0.820	5.863	0.90	0.240	4.40
Cu	1.316	0.287	1.517	0.11	0.141	0.77
Ni	0.344	0.123	1.583	0.18	0.057	0.33
Cr	0.309	0.041	2.460	0.19	nil	0.16
V	0.258	0.040	2.300	0.25	nil	0.33
Pb	0.210	0.041	2.829	0.040	0.44	0.011
Co	0.086	0.011	1.517	0.038	nil	0.110
Mo	0.085	0.037	0.057	0.004	nil	0.220
Cd	0.008	0.009	0.013	0.0006	nil	0.055
Hg	0.002	0.003	nil	0.0008	nil	0.017

Most of the metals migrate within the system of a large biological cycle whose major stages are the photosynthesis of the World's land vegetation and the degradation of dead organic matter by the microorganisms of the pedosphere. Significant metal masses are transported as components of stream suspensions and are almost completely lost into sediments.

The involvement of heavy metals in the biological cycle on land is concomitant with their selective differentiation. Noteworthy is the lack of proportionality between the quantity of the metals in the Earth's crust and their relative uptake by vegetation. The coefficient of biological absorption, K_b, for most metals varies from 1 to 9; for zinc, molybdenum, and silver, it is greater than 9, and for iron, vanadium, and chromium, it is less than 1. Because of the selective uptake of metals, their proportion in the vegetable biomass is significantly different from their proportion in the Earth's crust. Especially noticeable is the decreased ratio of iron to other metals. The biological cycle and differentiation of metals as effected by the photosynthetic organisms of the ocean exhibit specific features. The metal masses involved in the annual biological cycles on land and in the ocean are commensurate, although somewhat different in proportion. The World's land vegetation takes up more manganese and lead, and the photosynthetic organisms of the ocean, more molybdenum and cobalt.

Large masses of water-soluble and suspended metals are carried over from land to ocean in stream run-off. The coefficient of aqueous migration K_w for metals indicates that the most actively involved in aqueous migration are soluble forms of silver, mercury, zinc ($K_w > 10$), also molybdenum, cadmium, and copper, with their K_w ranging from 2 to 9. Ninety seven to ninety eight per cent of iron, manganese, chromium, vanadium, lead, and cobalt in the stream loss is transported in a suspended state. Besides, significant masses of dust-borne metals are blown away into the ocean by the wind. In turn, air-borne water-soluble metals are carried over from the ocean onto land. This process has as yet been but little studied, and no data for individual metals are available. Nonetheless, it appears that the migratory flux of heavy metals from ocean to land is much less intense than that in the reverse direction. For this reason, the annual metal cycles within the system "World's land-World's ocean" are essentially open. Large masses of metals are found in the sea and oceanic waters to become finally lost into bottom deposits. The recurrent involvement of deposited metals in mass-exchange cycles occurs owing to tectonic processes. In these processes, the mobilization of metals from sedimentary rocks is often more impeded than that from native crystalline rocks. The pedosphere performs the function of a global regulator for the migratory metals through keeping them at a definite level.

Gaseous organometal compounds escape from the ocean surface into the atmosphere. As has been noted in Chapter 3, higher plants exude volatile metal-containing compounds (terpenes, isoprenes). Still larger metal masses are released into the air as components of gaseous metabolites from bacteria. Of special importance are the processes of metal biomethylation. Minute soil particles, also containing metals, are entrained by the wind into the troposphere. All of those metal forms make part of the aerosols and are finally washed out by rainfall. However, the mass exchange between the land surface and atmosphere is as yet poorly understood, which makes the quantitative estimation of metal mass migration an arduous task for this cycle.

The pedosphere performs the function of a global regulator for the movement of heavy metal masses in the biospheric system of mass exchange. In the course of metamorphosis of organic matter, the metals, on their entry into the soil, make part of the mobile complex compounds and, simultaneously, become retained in the humus components. The most tightly held is mercury that is capable of forming stable complexes through binding to the functional groups of humic acids. Tightly held is also lead, less tightly copper, and still weaker, zinc and cadmium.The close conjugation of the migration cycles of heavy metals, as well as the role of the pedosphere as a global regulator of mass fluxes provide for a high stability of the biosphere as regards the additional supply of metals of both natural and technogenic origin.

7 Problems in the Organization of the World's Land Biosphere

7.1. Geochemical Inhomogeneity of the World's Land Biosphere

A global approach to the study of the biosphere as an integral whole presumes the maximally possible averaging of geochemical data for each of the biospheric components: sedimentary shell, ocean, atmosphere, and living matter. In reality, the World's land biosphere consists of a variety of spatially differentiated complexes encompassing compositionally different rocks, waters, and biocenoces. In studying separate territories, rather than the biosphere as a whole, we become aware of a geochemical inhomogeneity of the natural environment.

Two groups of factors determine the said inhomogeneity. The first group is associated with the compositional dissimilarity of rocks exposed on the World's land surface. The contrasts of compositionally different rocks are in part levelled-off by the layer of unconsolidated deposits on which the soil has built up. These deposits arise via denudation and redeposition of products of weathering, both of authigenic and allogenic origin. Depending on the proportion of authigenic and allogenic fragments and the specificity of their composition, the contents of chemical elements in the loose cover are seen to vary in a systematic manner.

Most of the redeposited products of weathering are composed of small fragments sizing 0.01 to 1 mm. These fragments originated in a variety of locations. In the northern European part of Russia clastic minerals translocated from the Baltic continental shield are predominant (Karelia, Finland, Kola Peninsula). To Zavolzh'e and Priural'e (Russia), the clastic material has advanced from the Ural Mountains. In the soils of Ukraine, there occur many clastic minerals constitutive of the rocks of the Ukrainian crystalline massif. The mineralogic and chemical composition of the allogenic rocks influences strongly the soil composition. For example, among the mineral clasts carried over from Karelia, quartz is abundant, whereas in the clasts originated from the mountains of Central Asia, the hypogene silicates (feldspar, mica, and others) are of more frequent occurrence than quartz. In the Ural region, the so-called green-stone rocks contain much epidote, actinolite, and chlorite are

very widespread. Of these, epidote is the most resistant one. For this reason, the deposits on which the soils of Priural'e were formed are enriched in epidote.

The change in the composition of soil-forming rocks affects the composition of soils, surface and underground waters, and also plants. For example, in the territory of the Estonian plateau, unconsolidated soil-forming rocks are profusely abundant in clastic limestone of Ordovician age, constitutive of the plateau basement. The abundance of calcium carbonates facilitates the formation of dark sward-calcareous soils as distinct from the podzolic soils typical of the adjacent regions. In the natural vegetation of the plateau, broad-leaved trees and herbaceous plants that require a large amount of nutritional calcium are widespread whereas in the neighbouring eastern regions, coniferous forests are dominant.

The local deviation of the concentration of a chemical element from its planetary crustal abundance is characterized by the clarke of concentration, C_c (see Section 2.5).

The concentration of most trace elements, especially of metals is in the unconsolidated covering deposits underlying the granitic crustal layer. This seems to be natural, since the covering deposits were formed by repeated redeposited products of weathering, partly depleted in chemical elements. At the same time, there are known regional geochemical specificities arising from the composition of the clastic rocks that form the covering deposits. For example, in the soil-forming rocks of the northern Kazakhstan, the concentration of titanium, lead, and copper is elevated as is strontium in Ustyurt; zirconium in the Russkaya Ravnina; and copper and cobalt in the Priural'e.

We have mentioned in Section 4.5 the data by Shacklette *et al.* (1984) according to which the soils and unconsolidated deposits of the Western States are distinguished by a higher concentration of heavy metals, whereas those situated east of 96° W, by elements typical of the crystalline rocks of the Precambrian basement (Nb, Zr, and others). Thus, the unconsolidated deposit cover and the pedosphere formed thereon are divided into vast mineral-geochemical provinces. By way of example, shown in Fig. 15 is a map of the mineral-geological provinces of soil-forming rocks in the European part of Russia.

Inside a province, the outcrop areas for deposits enriched in high-dispersed minerals are distinguished, as are the areas covered with sandy deposits. Each mineral is a host for trace elements with definite levels of concentration. In the sands of the Eastern European plain (Vostochno-Evropeiskaya ravnina, Russia), detrital quartz is predominant, with very low concentrations of all chemical elements except silicon. For this reason, the concentrational levels of elements in sandy deposits are lowered. In clay minerals that make up a fraction of particles sizing less that 0.001 mm, many trace elements occur at elevated concentrations. Our studies have provided evidence that in the European territory of Russia, the trace element concentrations in the loamy

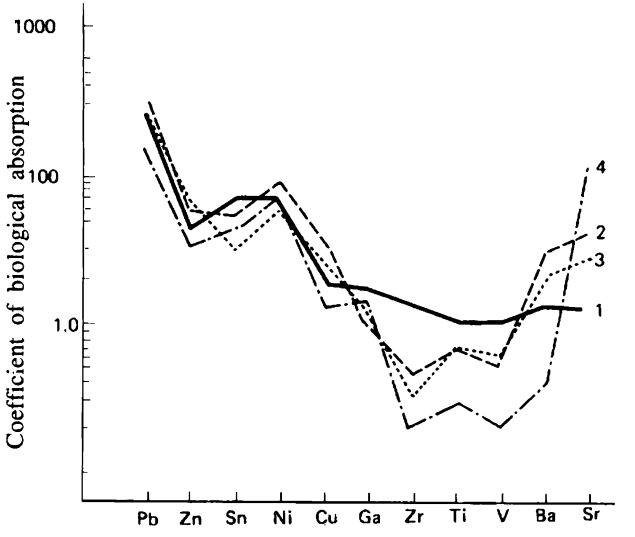


Fig. 15. Biological uptake of metals by typical plants of the Khibiny tundra (Dobrovolsky 1963)
1—linchens; *2*— mosses; *3*—grasses; *4*—rockfoil (*Saxifraga* species)

deposits are higher as compared to the sandy deposits: for vanadium, 1.0-1.5-fold; copper, 1.5-3.2-fold; nickel, 1.3-2.2-fold; gallium, 1.4-2.5-fold; titanium, 1.2-2.2-fold; and cobalt 1.9-2.0-fold. Besides, in the loamy soils and soil-forming rocks, the percentage of elements occurring in a sorbed state is significantly higher, which is an important factor for the involvement of these elements in the biological cycle.

The concentrational variations of elements in the original rocks and unconsolidated covering deposits determine the geochemical inhomogeneity of the World's land biosphere irrespective of the activity of living organisms. Simultaneously, the geochemical diversity of the pedosphere and loose continental cover is an essential factor in the development of the organic kingdom. Whatever is the concentrational deviation of a chemical element — either an increase or a decrease with respect to its crustal abundance — it will necessarily affect the biological element cycle and the composition of the local biota. Primarily, this refers to the plants that are in a straightforward manner dependent on the mineral supply from the soil and are responsive to its compositional variability.

The second group of factors contributing to the geochemical inhomogeneity of biosphere is associated with the activity of biogeochemical processes.

On the Earth's surface, the major source of energy for all processes is the radiant energy of the Sun. The supply of solar energy diminishes systematically from the equator to the poles; accordingly, the polar, temperate, subtropical, and tropical climatic zones of the Earth are distinguished. At first sight, one might have expected the activity of biological and biogeochemical processes to increase on passing from a cooler to a warmer climatic zone. However, the effective use of energy in chemical, physico-chemical, and biological processes is feasible only if sufficient water is available. According to Volobuev (1974), on the land surface, most of the energy (95 to 99.5%) is spent on the evaporation and transpiration of water by plants.

The expenditure on biological processes accounts for 0.5 to 5%, mostly about 1%. The hypergene metamorphosis of minerals requires hundredth and thousandth fractions of a percent of the total energy. The efficient use of the available solar energy by these processes is dependent on the degree of humidity: in arid regions, the efficiency is low, whereas in humid regions it reaches 70-80%.

The atmospheric humidification of the continental surface does not follow the pattern of climatic zonation. The annual amount and regime of atmospheric precipitation provide for varied humidity levels of the territories within a particular climatic zone. This entails a varied intensity of the aqueous and biological migrations of elements.

Most of the precipitated moisture, owing to the evaportranspiration, is returned to the atmosphere. The evaporated moisture controls the thermal conditions, which renders possible the existence of living organisms. The water cycle in a particular territory is of decisive importance for all types of migration of chemical elements.

The coefficient of relative humidity, K_h, is used as a quantitative estimate of this process. The K_h coefficient initially suggested by V.V. Dokuchaev and N.G. Vysotsky is currently defined as the ratio of the total precipitation to the evaporated moisture.

Volobuev (1974), on the basis of his analysis of the outcrop areas for soils of all types, has established the following ranges for the uniform relative humidity of landscapes:

Areas of uniform humidity	K_h
Very arid	< 0.20
Arid	0.20-0.40
Moderately arid	0.40-0.75
Moderately humid	0.75-1.20
Humid	1.20-1.95
Very humid	1.95-2.90
Extrahumid	> 2.90

The first three ranges are therefore characteristic of territories of various aridity, and the last three, of various humidity. The range with K_h of 0.75 to 1.20 delineates regions with an equilibrated water balance. Under the conditions of uniform relative humidity, the intensity of metabolism in landscapes and ecosystems increases with the solar energy supply (radiation balance). At low relative humidity of arid territories, the change in radiation balance is little felt. For this reason, the metabolisms in the extrahumid landscapes of high and low latitude share much in common. The situation is quite distinct in humid territories, where the increased relative humidity affects appreciably the radiation balance. This is the major reason for the difference of the mass exchange of chemical element in the humid landscapes of tropics and high latitudes.

A definite amount of rainfall water, not eliminated via evaporation and transpiration, becomes lost into run-off from the territory, intensifying thereby the aqueous migration of chemical elements. The run-off is determined not only by the precipitation-to-evaporation ratio, but also by a number of factors such as the relief, resistance of soils and soil-forming rocks to water, vegetation, rainfall regime, climatic conditions, and so forth. In most of the land, the run-off is $n \cdot 10$ to $300\text{-}400 \cdot 10^3$ m^3/km^2 per year; in extraarid regions, the rainfall is much smaller.

The masses of chemical elements involved in aqueous migration also show a large variability and are determined by the overall geographic conditions of a particular catchment area. The overall annual loss of chemical elements in the soluble form from plains and vast plateaus amounts to several tons or tens of tons per sq. kilometer, whereas in mountainous regions, it is tens to hundreds of tons per sq. kilometer. The stream loss of elements in suspension for plains is commensurate with the stream loss of soluble elements; however, under the conditions of considerable relief, the former loss is several times higher, and in mountainous regions, even by an order of magnitude above the latter.

The soluble forms of chemical elements are geochemically the most active run-off components. The extent of their involvement in aqueous migration is defined by the coefficient of aqueous migration K_w, which is the ratio of the concentration of an element in water to its concentration in the soil-forming rock of a particular region. This characteristic does not, however, apply to cyclic elements such as chlorine, as well as to elements which, subject to microbiological activity or evaporation, pass into a gas form and actively migrate in the atmosphere (sulfur, iodine, mercury). For most other elements, especially heavy metals, the use of the said coefficient seems to be justified enough.

In each particular region, the chemical elements have their K_w's characteristic. For convenience, the relationship between the chemical elements and the K_w coefficients is commonly represented in the form of appropriate graphs or histograms.

7.2. Intensity of Biogeochemical Processes on the World's Land

The humidity and temperature are major climàtic factors specific to any particular territory that affect the regime of the aqueous migration of elements in this territory and determine its flora and intensity of biogeochemical mass-exchange processes. The data summarized in Table 7.1 provide a dynamic characterization of the organic matter as synthesized by the major types o terrestrial vegetation.

The quantity of biomass provides, generally speaking, little information about the productivity of the vegetation types involved. In this respect, the annual growth is a much better characteristic of the efficiency of vegetable production. There is no direct proportionality between the phytomass and the annual growth. Along with these two, a very useful characteristic is what we shall conventionally refer to as the litter production, which is a quantitative measure for the annual die-off of vegetable material. The masses of organic matter as specified by the litter production and the annual growth are very close. These two indices characterize the synthesis and degradation of organic matter within the period of one year.

The litter-to-phytomass ratio indicates to what extent a particular type of vegetation is capable of retaining the synthesized organic matter. Apparently, a high retentive capacity is typical of the forests of the temperate climatic zone. For example, in the taigal spruce forests, only 2 to 4% of the organic matter of the phytomass is lost into sheddings, and in the oak forests, it is about 1.5%. In the humid rainfall forests, the sheddings account for 5% or even higher, whereas in the steppe vegetation, the annual die-off takes in almost all organic matter of phytomass.

The subsequent evolution of dead vegetable material in various biocenoses proceeds in a different manner. In tropical forests, the sheddings undergo a fast degradation, whereas in the forests of temperate climate, the degradation is never complete. For this reason, the soil cover in these forests accumulates a substantial amount (30-35 ton/ha) of dead organic matter, the so-called forest litter. In the tropics, the stored forest litter is tens of times smaller. In steppes, the percentage of dead organic matter is insignificant and tends to decrease with climate aridity.

The carbon dioxide cycle and the removal of carbon from this cycle in different vegetable assemblages may be characterized by the carbon accumulation factor which is defined as the ratio of the carbon, confined to unit area throughout the annual photosynthesis, to the amount of carbon released throughout one year from soil to atmosphere, by degradation of dead organic matter. Unfortunately, no experimental data are currently available on a direct

Table 7.1. Biological Productivity of Major Terrestrial Floral Biocenoses (after Rodin and Bazilevich 1965)

Biocenosis	Biomass, ton/ha	Annual growth, ton/ha	Litter production, ton/ha	Forest litter (peat felt), ton/ha
Arctic tundras	5.0	1.0	1.0	3.5
Low-bush tundras	28.0	2.5	2.4	83.5
Northern taigal spruce forests	100.0	4.5	3.5	30.0
Southern taigal spruce forests	330.0	8.5	5.5	35.0
Oak forests	400.0	9.0	6.5	15.0
Meadow steppes	25.0	13.7	13.7	12.0
Arid steppes	10.0	4.2	4.2	1.5
Half-shrub deserts	4.3	1.2	1.2	nil
Savannas	66.6	12.0	11.5	1.3
Rainfall humid forests	500.0	32.5	25.0	2.0

estimation of CO_2 production in the widespread vegetation assemblages. In a very tentative manner, one may presume that the extreme values of carbon accumulation factor refer, on the one hand, to humid rainfall forests and deserts (about 1) and, on the other hand, to tundras (4-5). Other floral assemblages will exhibit intermediate values.

One can form an idea of the proportion of carbon dioxide consumed in plant photosynthesis and confined to the soil in considering the accumulation factor for organic matter, K_o, defined as the ratio of the dead organic matter mass to the litter production. The more active the degradation of organic matter and the release of CO_2 is, the smaller is this factor. The data below are demonstrative of the statement:

Northern taiga and tundra	10 and higher
Southern taiga	5-10
Broad-leaved forests of temperate climate	2-5
Steppes of temperate climate	1-2
Deserts, humid rainfall forests	< 1

Plants as they synthesize organic matter release oxygen. The data, summarized in Table 7.2, provide a characterization of this activity for the major types of vegetation. The highest oxygen production is observed in tropical and

Table 7.2. Production of Oxygen in MajorTerrestrial Floral Biocenoses

Biocenoses	Carbon content in biomass produced, 40%, ton/ha	Carbon consumed in respiration, 15%	Oxygen production		
			on the basis of biomass produced, ton/ha	with allowance for consumption in respiration,	
				ton/ha	$10^3 \cdot m^3/ha$
Arctic tundras	0.4	0.06	1.08	1.24	0.87
Low-bush tundras	1.0	0.15	2.70	3.11	2.18
Northern taigal spruce forests	1.8	0.27	4.86	5.59	3.91
Southern taigal spruce forests	3.4	0.51	9.18	10.56	7.39
Oak forests	3.6	0.54	9.72	11.18	7.38
Meadow steppes	5.48	0.82	14.86	17.01	11.91
Arid steppes	1.68	0.25	4.54	5.21	3.65
Half-shrub deserts	0.48	0.07	1.30	1.49	1.04
Savannas	4.8	0.72	12.9	14.9	10.43
Rainfall humid forests	13.0	1.95	35.1	40.37	28.26

subtropical forests, and the lowest, in desert and arctic vegetations. The absolute value of oxygen production provides no genuine picture as to the contribution of some or other plant community to the enrichment of the atmosphere with oxygen. If the total of shed biomass throughout the year undergoes decomposition, then, accordingly, the total of oxygen released by photosynthesis becomes consumed, since a portion of oxygen produced can be retained in the atmosphere only on the condition that the dead organic matter is systematically accumulated in the pedosphere. It is to be inferred therefore that the most active floral biocenoses of the tropical forest type are not necessarily the most efficient producers of atmospheric oxygen. The chief "suppliers" of free oxygen on land are the landscapes of temperate and boreal zones where, owing to the inhibited microbiological processes, the dead organic matter is accumulated and stored.

The involvement of chemical elements in the biological soil cycle in various landscapes is as diversified as is the gas metabolism. In the meadow chernozem steppes, prior to human interference, over 0.2 tons of ash elements per hectar was annually involved in the biological cycle. In the southern taigal forests, this turnover was five times less.

As has been shown in Section 1.3, the extent of involvement of chemical elements from soil in the biological cycles is characterized by the coefficient

of biological absorption K_b. It should be kept in mind, however, that this coefficient, when referred to some elements, specifies not their entrapment from the soil-forming rock, but rather their overall supply to the plant organism from both atmosphere and soil. This is especially true of the cyclic elements and those migrating in the gaseous form. Nonetheless, for many of the chemical elements, this coefficient is a good measure for their entrainment from the soil-forming rock, soil, and soil water and their subsequent incorporation in a qualitatively different state of living matter.

The analysis of a large body of evidence has revealed a group of elements that are actively absorbed by all plants. This group includes manganese, zinc, molybdenum, copper, silver, and a number of others. Their K_b's are always greater than 1. The elements of another group are poorly uptaken by plants, their K_b's coming down to tenth and hundredth fractions of a unit. Such elements are zirconium, titanium, gallium, and vanadium. Finally, there are elements whose percentage in the plant ash is about the same as in the soil. Their K_b's are about 1. The features just mentioned bear relevance to the role the elements have played in the physiological and evolutionary processes.

It should be emphasized that, along with the general trends outlined, the natural conditions of a particular region are a very potent factor in the elemental uptake. By way of example, typical of the taigal vegetation is a sharp contrast in trace element accumulation reaching three orders of magnitude, or even more, whereas for other types of vegetation, this contrast is 10 to 100. Certain elements are actively taken up by the vegetation in some landscapes, and to a lesser extent in others. In particular, strontium is poorly absorbed by the vegetation of taiga and tundra, whereas in the vegetation of arid landscapes, its K_b is markedly higher over 1. Each type of vegetation in a particular habitat exhibits specific K_b's for chemical elements.

It should be noted that the magnitude of K_b is independent of the concentration of an element in the original rock, and is rather characteristic of the trend in the redistribution of the element in the natural complex and of the element exchange between the landscape components.

7.3. Elementary Landscape (Elementary Ecogeosystem) as a Basic Chorologic Unit of the World's Land Biosphere

The facts presented show the strong concentrational variability of chemical elements in rocks and soils and provide evidence for a drastic difference in the mass of elements which migrate in the surface waters of the Earth and become entrained in the biological cycle of various types of vegetation. The compositional and structural inhomogeneity of the biosphere

is especially characteristic of the natural environment of the World's land. Each continent and each particular region of the land are spatially nonuniform. By partitioning successively a territory into smaller parts, locations may be singled out, within whose confines a relative uniformity is maintained, which implies the same patterns for the relief, rocks, soil, vegetation, and microclimate. Such a locality, which is a chorologic (spatial) unit of the World's land biosphere, has been coined by Polynov (1956) the elementary landscape. For biogeochemical purposes, it may be regarded as the ultimate chorologic unit of the World's land biosphere and, simultaneously, as an elementary ecological geochemical system.

Thus, the elementary landscape is the ultimate natural territorial complex whose all components (soil-forming rocks, soils, surface and underground waters, living organisms, atmosphere) are interrelated via cyclic mass-exchange and metabolic processes. The selective mobilization of chemial elements is effected owing to the biogeochemical activity of living organisms. In turn, the elementary landscapes (elementary ecogeosystems) are intimately interrelated via elemental mass fluxes operated through the agency of the atmosphere or aqueous migration on the land surface. Two groups of elementary landscapes are distinguished by the character of interlandscape links.

The intralandscape mass exchange between the components of an elementary ecogeosystem situated on the elevated parts of landscape is comparatively independent of the neighbouring elementary landscapes. The mass exchange with the surrounding territory is maintained only through the tropospheric mass transport. Such elementary landscapes are referred to as the geochemically autonomous ones.

A distinctive feature of all cyclic elemental mass-exchange processes in the biosphere, including the global cycles and those occurring within an elementary ecological geochemical system, is their openness. Therefore, the masses of elements that leave some or another mass-exchange cycle in an autonomous landscape are transported by surface or underground waters to the adjacent landscapes situated at lower relief levels. This transport is unidirectional and is effected via migratory mass flux. Elementary landscapes systematically supplied with additional run-off masses of elements are referred to as the geochemically subordinate ones.

The masses of chemical elements as transported from autonomous landscapes become involved in the biogeochemical processes occurring in geochemically subordinate ecogeosystems. The mass-flux-mediated connection within a sequence of elementary landscapes located at different relief levels is currently known as the geochemical conjugation. This phenomenon is of widely spread occurrence. This may be exemplified by the connection between low and raised peatlands, previously referred to in Section 4.3. Owing to the geochemical conjugation, the river floodplains of the forest zone are supplied with additional

masses of compounds of nitrogen, phosphorus, potassium, calcium, and other numerous trace elements accessible to plants and carried off the river catchment area. In steppes, at the bottom of shallow relief depressions, small-sized globular concretions of iron and manganese oxides occur, formed by these elements as they were carried from the surrounding landscapes. In tropics, on low-land seasonally water-logged plains, massive laterite plates are formed in a similar manner.

The geochemical conjugation exerts a very strong influence on the biological cycling. In the vegetation of subordinate landscapes, the concentration of ash elements is several times higher as compared to the autonomous landscape vegetation. In certain cases, the concentration of the chemical elements supplied via geochemical conjugation may reach high levels leading to detrimental effects. For instance, in Vietnam, profuse rains precipitated in the mountainous regions facilitate the active leaching of fluorine out of rocks. This element is washed down to surface waters; in the mountainous regions, its concentration is small and presents no health hazard for the population. The run-off waters, as they reach the coastal plains, undergo intensive evaporation with the resultant increase of fluorine concentration above the allowable level. This causes numerous diseases in the coastal population, such as the tooth enamel decay and acute forms of fluorosis.

7.3.1. Typomorphic Elements and the Biogeochemical Formulas of Elementary Landscape

By virtue of the fact that the geochemical conjugation is effected owing to the aqueous migrations, the chemical elements influence this process in an unlike manner. Of prime significance are the gaseous compounds — carbon dioxide, oxygen, and hydrogen sulfide, produced by biotic activity of organisms. The gases dissolved in natural waters determine the oxidation-reduction conditions essential for the solubility of many chemical elements, mostly metals. In the river floodplains, water-logged relief depressions and the similar geochemically subordinate landscapes, under reduction conditions in the presence of hydrogen sulfide, there are formed insoluble sulfides of iron, zinc, copper, lead, nickel, cobalt, silver, cadmium, and mercury. In an oxygen-free medium devoid of hydrogen sulfide and rich in carbonic acid, most of these elements are active migrants. In an oxygenated medium, metals form higher oxides which with most metals, for example, iron, manganese, cobalt, are insoluble.

Quite important also are elements capable of passing in large amounts into surface and soil waters, providing thereby for acid-basic conditions that may affect dissolution or precipitation of other elements. The former elements are referred to as typomorphic.

For an element to be typomorphic, it must be, first, abundant. For this reason, typomorphic are most commonly the major chemical elements. Second, the element must persist in a form enabling its transition into a soluble state. For instance, certain landscapes are very rich in quartz. Silicon, constitutive of the resistant and stable structure of this mineral, is released with difficulty, its concentration in natural water is very low and therefore, despite its abundance in the landscape, it can affect but little the composition of plants and soil solutions. Third, the typomorphic elements must be prone to accumulate in a subordinate landscape. If the element is transiently migratory, its participation in the geochemical conjugation is rather limited. For example, substantial masses of chlorine migrate actively in both autonomous and subordinate landscapes of the taigal forest zone. However, in deserts, owing to intensive evaporation, the concentration of this element is high, and quite often it plays a leading role in the geochemical conjugation of landscapes.

The trace elements involved in biological or aqueous migration, cannot be typomorphic because of their small content. However, they determine the elemental redistribution within a landscape, and for this reason are referred to as the indicator elements. The crustal abundance of trace elements is less than 0.01%. These elements, when present in concentration exceeding their crustal abundance hundreds and thousands times, can play a typomorphic role. Such a situation is exemplified by ore deposit outcrops, where the trace elements occur in markedly high concentrations.

The existence of an elementary landscape and the performance of an elementary ecogeological system are feasible only owing to the exchange and redistribution of chemical elements. Therefore, the elementary system can be described in quantitative terms of chemical element redistribution among the landscape components.

The elementary landscape (elementary ecogeosystem) has an initial reserve of chemical elements contained in the soil-forming rock. An estimate of the initial reserve for each element is given by the clarke of concentration C_c. Due to the processes occurring in the soil, part of the chemical elements acquire mobility and become thus involved in the aqueous migration and biological cycling. Quantitatively, these migrations are tractable in terms of elemental redistribution indices, first, between the original soil-forming rock and vegetation (in terms of K_b) and, second, between the original soil-forming rock and natural water (in terms of K_w).

In reference to the above, any elementary landscape may be characterized by a biogeochemical descriptive formula of the form $A(G)\frac{B_i}{B_j}$, where A stands for the typomorphic element, and the parenthetic G for a gas dissolved in water; B_i (i = 1, 2, ...) designates elements for which $K_b > K_w$; accordingly, B_j (j =

Table 7.3. Geochemical Landscape Coefficients for Autonomous and Subordinate Landscapes of the North-Eastern Predkavkaz'e

Landscape	Chemical elements							
	Mn	Cu	Zn	Pb	Mo	Sr	Ba	Ti
	Coefficient of biological absorption							
Steppe piedmont plain	1.0	4.0	3.5	0.8	10.0	1.8	1.0	0.5
Alluvial meadow valley	3.0	9.0	6.0	1.8	6.0	1.5	3.5	0.6
	Coefficient of aqueous migration							
Steppe piedmont plain	0.3	0.1	1.0	0.3	1.0	4.1	1.0	0.2
Alluvial meadow valley	3.5	3.0	3.3	2.5	0.5	1.2	1.5	0.2

1, 2, ...) designates elements for which $K_b < K_w$. Thus, for a particular landscape, two main groups of indicator elements contributing to the geochemical conjugation are distinguished, one group including elements actively involved in the biological cycle, and the other group, those involved in the aqueous migration. In addition, in order to distinguish an autonomous elementary landscape from a subordinate one, in the descriptive formula of the latter, the typomorphic element is labelled with the left-side superscript asterisk, e.g. *A(G).

The formula $Ca^{2+}(O_2)\frac{Mo, Cu, Zn, Mn}{Sr}$ designates an autonomous elementary landscape in which the redistribution of chemical elements occurs in the presence of calcium ions at high concentration in the surface waters and with a free access of oxygen, that is, in a weekly alkaline oxidative medium. The most actively involved in the biological cycle are molybdenum, copper, zinc, and manganese, whereas strontium is an active migrant in the surface and underground waters.

Let us consider, as an example, a certain location in the territory of north-eastern Predkavkaz'e (submountain Caucasus). In this region, the meadow landscapes of alluvial valleys are subordinate geochemically to the autonomous landscapes of high piedmont plains. The typomorphic element is calcium, and indicator elements are manganese, copper, zinc, molybdenum, strontium, and, in part, lead and barium. Certain chemical elements behave indifferently toward the intralandscape exchange and cannot therefore be regarded as indicator elements. The typical representative is titanium whose characteristics are featured in Table 7.3. In well-drained high plains, the atmospheric air penetrates

freely into the soil and soil-forming rocks favoring thereby the creation of oxidation conditions.

Because of the high level of underground water that periodically sets in due to the overland run-off, the meadow landscapes experience deficiency in oxygen. This results in the buildup of more or less gleyed soils, with the concommitant concentrational rise of certain metals, in particular, manganese, in the soil water. The available evidence has allowed to suggest a formula for the meadow landscape in question:

$$*Ca^{2+}(Co_2)\frac{Cu, Mo, Zn, Ba}{Mn, Sr}$$

The steppe landscape formula for high piedmont plains has been given above.

To briefly summarize the problem of the World's land biosphere organization, we may say that the global system of biosphere is based on a cyclic mass-exchange of chemical elements. The mass-exchange cycles are open, which provides for the simultaneous performance of a variety of cycles of different rank. The decisive role in the global mass-exchange system belongs to biogeochemical processes, and the basic chorologic unit of the World's land biosphere may be defined in terms of elementary landscapes (elementary ecogeochemical systems).

The potential mobilization of chemical elements by living matter for their involvement in the mass-exchange cycles increases with the supply of solar energy from the poles toward the equator. The implementation of this potentiality is dependent on the atmospheric humidity. The biogeochemical mobilization of elemental masses can be effected either completely in accordance with the temperature conditions, or in part because of the atmospheric moisture deficiency. A definite combination of temperature conditions and atmospheric humidity determine the zonality of biogeochemical processes as an important factor in the biosphere organization.

8 Biogeochemistry of Polar Zone

The polar landscapes not entirely devoid of plants occur only in the Northern Hemisphere. Among them, arctic landscapes and tundra landscapes are distinguished. The former occupy a total area of $706 \cdot 10^3$ km^2, whereas the latter extend to a larger space of $3756 \cdot 10^3$ km^2.

8.1. Biogeochemistry of Arctic Landscapes

The conditions for biogeochemical processes in the Arctic are quite peculiar. Because of the climatic severity, the arctic vegetational season is very short; the perennially frozen ground (permafrost) underlying the upper soil cover at a depth of 40-45 cm provides for a very small volume within which the plants can interact with the mineral substrate. Thus, the biological cycle of chemical elements is limited in both time and space.

The arctic land, represented by islands and archipelagos, is strongly exposed to the ocean. The arctic basin is separated from the warm streams of the Pacific and Atlantic oceans by continents and submarine ridges. Along the Eurasian continental shelf from the Chukotski peninsula westwards, the cold Transarctic stream flows; its counterpart stream flows eastwards along the North American shelf. North-east off Greenland, the two streams meet to merge into a current that starts moving southwards. Near Iceland, this current meets with the warm North Atlantic stream. At the region where these two powerful countercurrents meet, cyclones are generated which move eastwards along the polar ice frontier giving off continuously heat and moisture. A significant part of moisture is precipitated over the western coast of the Svalbard Archipelago, mostly over the western coast of its largest island Spitzbergen, where the mean rainfall is 400 mm/year. Eastwards, on Franz Josef Land, the rainfall is 200-300 mm/year. Still further eastwards, on Severnaya Zemlya, it is 100-200 mm/year. Simultaneously, the average temperature of the air in winter lowers from west toward east. Likewise, a severe climate is typical of the islands of the North American Arctic Archipelago and of the northern and north-western coasts of Greenland, where the rainfall is 100-200 mm/year, and the temperature in January is –30° to –38° C.

Owing to the prevalent climatic conditions, most arctic land has turned into a peculiar polar desert. The small atmospheric precipitation and the water persisting in solid state during 10-11 months of the year have led to the development of features typical of arid landscapes: the alkaline soil reaction (pH 7.5-8.0) and even the occurrence of recent carbonate formations (Tedrow 1968).

The most favorable conditions for biogeochemical processes are provided for in the western part of Spitzbergen. Owing to its more moderate and moist climate, the regions with vegetative cover extend to a larger area than in other arctic islands. Three types of landscapes (Dobrovol'sky 1989) are widespread. On the wide shore terraces of fiords and on the sloping proluvio-soliflual accumulations at the base of piedmonts grows the vegetation of arctic tundras. It is represented by mosses and lichens interwoven with the twigs of arctic willow (*Salix polaris*), varieties of rockfoils (*Saxifraga oppositifolia, S. polaris, S. caespitosa*, etc.), dryad (*Dryas octopetala)*, specimens of arctic poppies, buttercups, cinquefoils, various tufted rushes (*Juncus*) and grasses. In some territories, the vegetation forms a continuous covering and in others, it is confined to depressions enclosing cryogenic polygons. The carpet of matted plants closely overlying the soil surface constitutes the uppermost A_0 horizon of the soil profile. The soils are brown arctic tundral, with profile of the *A/C* type.

In high plateaus (over 400-500 m above the sea level), the vegetational soil cover is sparse, its surface coverage being less than 10%. Among the plants short-growth mosses growing on shallow-soil accumulations at the center of medallions or in depressions at the periphery of polygons are predominant. Lichens grow on mosses and large rock fragments. There occur separate specimens of rushes and rockfoil. The soils are of the arctic fragmentary (coarse skeletal) type.

On the flat, variously water-logged bottoms of glacial valleys opening onto fiords, the vegetation is mainly represented by rank hypnic and sphagnic mosses. In relatively dry sites, cassiopes (*Cassiope tetragona*), tufted grasses and rushes grow. Such conditions are favorable for the formation of peat, but the thickness of the peat layer is very small because of the close vicinity (40-45 cm) of permafrost. In wide valleys, there occur small thermokarst lakes bordered by sedges (*Carex nordina, C. rupestris*), cottongrass (*Eriophorum*) and nappy plant.

The ash analysis of peat-forming plants (mosses) and of peat has revealed the predominance of silicon among the ash elements. Silicon is particularly abundant in the sphagnum (36.5% by ash weight). The next in order are iron and aluminum. Iron accumulates during the course of peat formation. Both in the living moss and in peat, calcium occurs in a larger amount than sodium; also, potassium predominates over sodium. One should note an appreciable

amount of sulfur. A large amount of mechanically admixed mineral particles (40 to 80% by ash weight) is found in mosses. This is due to the deposition of finely-dispersed mineral material which is carried in the melting glacier water and, in part, to the fall-out of atmospheric dust. The content of mechanical mineral admixture in peat is 60 to 80% by ash weight.

The plant species of common occurrence mentioned in the characterization of landscape environments have been analyzed for heavy metal contents. The relevant data are summarized in Table 8.1.

One will observe that the terrestrial plants differ from the littoral algae in a markedly higher concentration of metals and a lower concentration of sea salt cations. A higher level of these cations is also characteristic of the coastal plants (specimen 45) or those growing at the tide line (specimen 55a).

The data on the ash content of plants merit a special discussion. The commonly accepted view that arctic plants exhibit a very low ash content requires some comment. The fruticose lichen growing in rock fissures has an ash content of 1.39-2.80% (on an air-dried weight basis), whereas in the mosses of the same habitat, the ash content is 2-3 times higher. The ash content of the leaves of arctic willow is 3.22 to 4.57%, whereas that of rockfoils growing in close vicinity is 7.50 to 9.25%. The difference in ash content is still more marked in plants of different habitat. For example, the ash contents of the aerial parts of rushes collected in the high plateau Hogfjellet is 6.22% and that of the same species from a neighbouring glacial valley is 10.87%. The ash content of mosses growing on mountain slopes is 5.08%, in the terrace of a glacial valley, 8.64%, and in the water-logged bottom of the same valley, 15.6%.

The high ash content of Spitzbergen plants and, presumably, those from other regions of the arctic land is due to the mechanical admixture of finely-dispersed mineral particles, either air-borne or deposited onto plants from thawing water. For this reason, the experimentally determined ash content (% of ash on a dry organic matter basis) and the sum total of ash elements making part of the plant tissue (% of material extractable from the ash by 1 N HCl) differ appreciably. As has been noted above, a particular high amount of mechanically admixed mineral particles is contained in the vegetation and peat of glacial valleys, the major route for thawing water run-off: in moss, 40 to 80% by ash weight, in peat, 60 to 80%.

The data in Table 8.1 show that the highest concentrations are typical of iron amounting to hundreds and thousands of micrograms per gram of dry vegetable matter; for zinc, tens of micrograms per gram are common and for copper, a few micrograms per gram. A very large spread in values, from several units to the first hundreds of micrograms per gram, has been found to occur for manganese. Against a background of these general trends, one will observe a geochemical specialization of separate systemic groups. For example, characteristic of the rush species is the relatively high concentration of iron

Table 8.1. Concentrations of Heavy Metals and Sea Salt Cations in the Plants of Spitzbergen (Dobrovolsky 1989)

Plant and sample No.	Concentration of chemical elements, μg/g, by dry plant weight									
	Fe	Mn	Zn	Cu	Pb	Ni	Co	Na	K	Ca
Lichens										
9	138.6	6.2	10.0	2.5	7.8	< 1.5	< 1.5	633.3	2000.0	1170.0
12	713.1	4.2	36.7	4.2	8.3	< 1.5	< 1.5	308.3	3750.0	370.0
Mosses										
10	1240.0	13.9	8.3	5.2	5.8	1.7	< 1.5	866.7	2170.0	758.0
62	2273.1	238.5	45.1	6.7	10.0	7.6	2.7	325.0	1670.0	193.0
34	6320.7	52.6	15.3	3.8	13.5	5.5	2.6	4696.9	2273.0	3636.0
30	4712.7	100.5	36.7	6.2	2.0	14.5	2.0	291.7	2080.0	425.0
Rockfoils (aerial parts)										
5	1751.0	44.3	50.8	8.8	< 1.5	2.6	< 1.5	1833.3	10000.0	1460.0
11	946.9	76.6	28.4	3.7	1.6	< 1.5	< 1.5	1125.0	4580.0	1375.0
Arctic willow (leaves and current twigs)										
24	400.8	87.8	176.2	8.0	2.7	3.7	< 1.5	658.3	6670.0	1375.0
25	nil	83.2	85.7	5.8	1.7	< 1.5	< 1.5	425.0	7080.0	2420.0
61	240.0	262.2	161.9	7.0	1.5	5.5	< 1.5	226.0	8330.0	525.0
Cotton grass (underground parts)										
39	nil	nil	90.0	7.3	1.5	2.5	1.5	441.7	20000.0	683.0
Rush (aerial parts)										
31	1380.0	286.0	63.5	5.8	1.5	4.3	1.5	275.0	667.0	400.0

33	1060.0	250.0	80.1	7.8	1.7	9.5	1.8	333.3	4580.0	458.0
36	nil	nil	nil	5.1	3.1	4.3	1.5	441.7	7500.0	550.0
46	1563.1	353.9	76.8	6.7	1.5	3.4	1.5	808.3	10830.0	858.0
Alpine sorrel (stem and roots)										
45	3480.0	172.0	24.5	8.9	1.8	16.7	1.5	2000.0	8330.0	1550.0
Heather										
55a	1659.0	106.2	35.6	10.5	1.5	3.7	1.5	10500.0	22500.0	9580.0
Laminaria										
8a	202.8	15.0	16.6	3.7	1.5	1.5	1.5	2033.3	4330.0	6000.0
47	73.6	2.7	11.7	2.8	1.5	1.5	1.5	25330.0	48330.0	24330.0
55	nil	60.3	28.4	5.5	1.5	5.5	3.3	48000.0	22500.0	17580.0
55b	556.1	44.6	27.6	10.3	4.2	1.5	1.5	13330.0	11670.0	18000.0

Species and sampling site: 9, *Cetraria nivalis*, fragments of crystalline slate, Gashamna, Hornsunn; 12, *Umbricaria arctica*, sampling site the same; 10, *Rhacomitrium hypnoidos*, sampling site the same; 62, hypnaceous mosses, structural terrace, Reindalen; 34, gray mosses, high plateau (610 m), Hogfjellet; 30, tussocky gypseous moss, Gröndalen; 5, *Saxifraga oppositifolia L.*, glacial moraine, Hansoreen; 11, *Saxifraga hirculus L.*, Gashamna, Hornsunn; 24, *Salix polaris Wahl*, low sea terrace, beach scarp, Hornsunn; 25, sampling site the same, 1 km distant from coast line; 61, structural terrace, Reindalen; 39, *Eriophorum*, low terrace, Isfjorden; 31, isolated vegetation bed, water-logged bottom, Gröndalen; 33, sampling site the same, sea coast of Granfjorden; 36, high plateau, Hogfjellet; 46, low terrace, Isfjorden beach scarp; 45, beach, Van Mijenfjorden; 8a, dry blades of laminaria, Hornsunn fiord; 47, laminaria collected from the bottom during tidal fall, Isfjorden; 55 and 55b, laminaria blades of different degree of dryness, Van Mijenfjorden beach.

(1060-1563 μg/g) and manganese (250-354 μg/g); lichens are high in lead (7.8-8.3 μg/g); arctic willow, in zinc (85.7-176.2 μg/g) and copper (5.8-8.0 μg/g). The plants confined to geochemically subordinate conditions (in glacial valleys) are distinguished by an elevated concentration of one or a few more metals. A particularly elevated concentration of copper, manganese, and lead has been recorded in the mosses growing in the water-logged bottoms of valleys. Also, an elevated concentration of some metals has been observed in plants growing in an immediate vicinity to the coast line. Thus, in an arctic willow (specimen 24) distant a few meters from the tide line, the level of zinc, copper, lead, and nickel was higher as compared to that of a plant of the same species (specimen 25) distant 1 km from the coast line and sheltered from the sea by a morainal hill. Simultaneously, the coastal plants contain more of sea salt cation (specimens 45, 55a).

The effect of the ocean is not merely confined to a transport of heat and moisture. Carried over in the air masses are also oceanic aerosols, mostly composed of water-soluble salts. The aerosols are actively "washed-out" by snow precipitation. According to the available evidence, an average of 5 tons of sea salt per square kilometer per year is precipitated from the atmosphere over the northern coast of the European part of the USSR; in Franz Josef Land, it is 3 tons per square kilometer per year. As reported by Evseyev (1988), the mineralization of snow precipitation in the Arctic is close to 10 mg/liter. Consequently, given the annual precipitation 400 mm, about 4 tons of sea salt per square kilometer per year is deposited over the western territory of Spitzbergen.

Predominant in the composition of oceanic aerosols are water-soluble sulfates and chlorides of alkali and akaline-earth elements. An important factor is the permanent occurrence therein of heavy metals in negligibly small amounts. The origin of these components has not yet been clarified completely; however, the ever-increasing body of facts provides evidence that in regions remote from industrial centers, the metal concentration is determined by natural factors, and the presence of metals in the troposphere should be regarded as a natural phenomenon similar to their occurrence in the World's ocean or in the Earth's crust.

The heavy metals in snow deposits and glaciers of the Arctic and Antarctic have been an object of intensive studies during the last 30 years. At present, it is a well-established fact that the metal concentrations in snow precipitation of the two polar zones of our planet differ among themselves. For one thing, this difference must be attributed to natural factors. The composition profile studies of Greenland glaciers have shown that the metal concentrations in recent and ancient glacial layers are not inordinately different. Actually, a 3-to-4-fold rise in concentration may reasonably be presumed only for zinc and lead (Boutron 1978; Herron *et al.* 1977; Weiss *et al.* 1978). The actual contribution

due to oceanic aerosols should be regarded as a natural link in the global biogeochemical cycle of heavy metals.

The supply of oceanic aerosols gains a special importance under the conditions of arctic landscapes, where the interaction between the vegetation and mineral substrate is significantly inhibited, and the hypergene degradation of minerals is suppressed. According to the data by Evseyev (1988), the following metal concentrations (in μg/liter) are typical of the Spitzbergen snow cover: Fe, 27.5; Mn, 0.80; Zn, 31.1; Cu, 1.7; Pb, 0.9; Ni, 0.3; Co, 0.3. It seemed expedient to compare these data with the contents, in the soil-forming rocks, of mobile metal forms that can be mobilized and involved in the biological cycle. For that purpose, metal concentrations have been determined in extracts, using water and 1 N HCl solution, from the widespread soil-forming rocks —loose products of cryogenic metamorphosis of the local original rocks. The relevant data are summarized in Table 8.2.

As is seen in Table 8.2, the concentrations of the water-soluble metal forms that can be directly involved in the biological cycle are rather low. The arctic climatic conditions and the permafrost not only put a limit on the interaction of plants and mineral substrate, but are also inhibitory to the processes of hypergene destruction of minerals. As to the forms mobilizable by the action of weakly acidic soil solutions, their concentration is a hundred times superior to that of iron and manganese in snow, whereas for other metals, this excess

Table 8.2. Concentration of Mobile Forms of Heavy Metals in Loose Deposits of Spitzbergen

Extraction	Concentration of chemical elements, μg/g						
	Fe	Mn	Zn	Cu	Pb	Ni	Co
Aqueous extract (n = 10)							
M	5.71	0.54	0.53	0.11	< 0.05	0.07	0.03
σ	4.64	0.28	0.21	0.08	—	0.08	0.03
V, %	81	52	40	73	—	107	100
1.0 N HCl extract (n = 16)							
M	1266.6	408.8	7.41	4.64	4.23	0.83	1.04
σ	949.3	148.0	2.40	2.46	2.23	1.07	0.45
V, %	75	36	32	53	53	129	43

Note: n is the number of analyses; M is the arithmetic mean; σ is the root-mean-square deviation; V is the coefficient of variation.

is not too great. The above data show therefore that the atmospheric precipitation in Spitzbergen is an important source for the supply not only of sea salts, but also of certain metals.

The supply of sea salt and trace elements via precipitation appears to contribute to the elevated concentration of water-soluble forms of alkaline and earth-alkaline elements and heavy metals in the uppermost vegetable soil layer.

Certain amounts of metals become retained in peat and in the dead organs of plants and are thus eliminated from the biogeochemical migration cycles. Taking into account the thickness of peat accumulations, however small they might appear, in the hydromorphic soils of Spitzbergen, one may come to the conclusion that the peat stores an appreciable amount of mobilizable forms of iron and manganese and a smaller reserve of other metals.

In the matted cover of densely intertwined tundra, essentially mossy vegetation inseparable from the dead organic matter, the uptaken metal compounds undergo complex transformations. The proportion of different metal forms may be exemplified by the results of a study of iron and zinc contained in the vegetative cover and peat accumulations of the flat tundra, in the low terrace of Isfjorden and in a water-logged depression of the same terrace (Dobrovolsky 1990).

As revealed by dialysis studies, the soluble forms of iron and zinc accounted for about 80% of the total of these metals found in solution. In the upper peat layer with living plants, sampled from the water-logged depression, the soluble forms of iron were about 70% and of zinc, about 50%; in the underlying peat layer, the percentage of both forms tended to decrease. A similar tendency was recorded for soluble forms of carbon: on passing from the vegetative to the peat layer, their percentage decreased two-fold in the terrace and still greater, in the water-logged depression.

Electrodialysis of the soluble forms of iron has revealed the predominance of electroneutral forms. A similar distribution holds also for carbon, which provides a good reason to presume that the electroneutral forms are represented by organic iron-containing species. Among the soluble zinc forms, the percentage of electroneutral forms is somewhat lower than that of charged forms, with the anions present in a larger amount in the upper vegetative layer.

The data obtained indicate that the upper vegetative peat layer of the arctic Spitzbergen tundra contains a larger amount of soluble forms of metals. Among these forms, the proportion of positively and negatively charged forms and neutral forms is not the same for different metals. Only a certain part of the soluble forms, mainly those positively charged, is involved in the biological cycle. Most of these are either lost to water run-off, or retained in the peat, from where they can be remobilized by the action of acidic plant metabolites. The concentration of metals as taken up by peat is tens and hundreds times higher above the concentration of soluble forms.

The different metal uptake by plants leads in a natural way to different involvement of metals in the biological cycle. A comparison of the metal concentration in plants and the metal concentration in aqueous extracts from soil-forming rocks reveals that iron and manganese are the most actively absorbed by plants, with the plant-to-soil metal concentration ratio falling within a range of $100n$ to $1000n$. For zinc, copper, and nickel, this ratio is of the order of $10n$. It is noteworthy that the high concentrations of iron and manganese tend even to increase in the dead organic matter.

The systematic removal of metals via run-off and their uptake from solution by the dead organic matter are continuously counterbalanced by the new supply of mobile metal masses, which maintains the biological cycle and performance of the ecogeosystem of arctic tundra *in toto*. The main sources of water-soluble metal forms are oceanic aerosols precipitated from the atmosphere as well as soil-forming rock minerals containing trace elements.

The available body of evidence allows, as a first approximation, to estimate the migratory masses of heavy metals in the arctic tundra of Spitzbergen. Based on the above-cited data about the metal concentration in snowfall, the supply of metals on the western sea-coast of Spitzbergen can be estimated as follows (in g/year per 100 mm of precipitation): iron, 27.5; manganese, 0.8; zinc, 31.1; copper, 0.9; nickel, 0.3. It is of interest to compare these values with the masses of metals involved in the biological cycle and those contained in the phytomass and dead organic matter of arctic tundras.

As reported by Tishkov (1983), the total mass of living plants in the tundra vegetation grown on the low terrace in the region of Barentsberg is 2.9 ton/ha by dry weight; accordingly, the mass of dead plant matter, 9.6 ton/ha, and the annual growth (productivity), is 0.6 ton/ha. To be noted for comparison, the annual growth for arctic willow (*Salix arctica*) growing in isolated vegetation beds in Cornwallis Island (the Canadian Arctic Archipelago, 75° N) is a mere 0.03 ton/ha (Warren W. 1957). Based on these data and on the average heavy metal concentrations as determined by us for the tundra vegetation of the western Spitzbergen seacoast, a distribution of metal masses is given in Table 8.3. The supply of metals in precipitation has been calculated per 300 and 400 mm/year, in accordance with the precipitation rate in the western Spitzbergen sea coast.

One will observe in Table 8.3 that for iron and manganese, the metal mass in the annual growth is an order of magnitude higher than that supplied through precipitation. Simultaneously, for other metals, for example, copper, the tropospheric metal supply is quite enough to provide for the growth requirement in metals and thus to ensure a normal performance of the ecogeosystem of arctic tundra. The more so, the tropospheric supply of zinc and lead is even in excess of the "norm" for the uptake of these metals into the biological cycle.

Table 8.3. Mass Exchange of Heavy Metals in the Ecogeosystem of ArcticTundra of Spitzbergen (Dobrovolsky 1989)

Metal	Rounded-off average concentration in vegetation, μg/g, by dry weight	Metal mass, grams per hectare			Metal supply in precipitation, g/ha per year
		in living phytomass	in dead organic matter	in annual growth	
Fe	2000.0	5800.0	19200.0	1200.0	82.5-110.0
Mn	150.0	435.0	1440.0	90.0	2.4-3.2
Zn	60.0	174.0	576.0	36.0	93.3-124.4
Cu	6.3	18.3	60.5	3.8	5.1-6.8
Ni	4.3	12.5	41.5	2.6	0.9-1.2
Pb	3.7	10.7	35.5	2.2	2.7-3.6
Co	1.0	2.9	9.6	0.6	0.9-1.2

Presumably, this fact is indicative of an elevated concentration of these metals in the arctic troposphere. However, this situation does not cause a disfunction within the ecogeosystem. The regulation of migratory fluxes in the soil involves, *inter alia*, the formation of metal compounds accessible to plants or capable or migrating in run-off. Excess amounts of metals are in part taken up by the dead organic matter, or part of them is lost in run-off. Judging by the concentration of lead accumulated in water-logged peatlands, a significant part of this metal is held in the dead organic matter as distinct from zinc, most of which is washed away in run-off.

The ecogeosystems of water-logged glacial valleys, geochemically subordinate to the landscapes of arctic tundra, receive in surface run-off an additional quantity of nutritional mineral elements, heavy metals included. This results in a 3-to-4-fold increase of the annual growth as compared to the vegetative productivity of arctic tundras and in the corresponding increase of metal masses involved in the biological cycle. In turn, the high productivity of bog moss vegetation facilitates the accumulation of an appreciable quantity of dead organic matter enriched in heavy metals, particularly iron and manganese. The following estimates of metals stored in the peat of water-logged valleys have been made: iron, tens of kilograms per hectare; manganese, 1-2 kilograms per hectare; zinc, 100-300 grams per hectare; copper, lead, nickel, tens of grams per hectare.

Biogeochemistry of Tundra. The tundra landscapes occupy the farthermost northern strip of the continental land bathed by the seas of the Arctic basin.

The climatic conditions of the tundra zone provide for a higher activity of biogeochemical processes as compared to the Arctic. The vegetation of tundra is represented by mosses, lichens, herbaceous plants and shrubs of varied size. Northwards mosses and lichens are predominant, and southwards, shrubs.

The edaphic microflora is diversified, and the community of microorganisms is more numerous than that of the arctic soils. The bacterial population varies from 500 to $3500 \cdot 10^3$ specimens per 1 gram of top soil horizon.

The contents of the total of ash element and of nitrogen in the tundra biomass are roughly the same. Among the ash elements, the highest concentrations are typically of calcium, potassium, magnesium, phosphorus, and silicon. The concentration of other elements seldom exceeds 0.1%. In the underground parts of plants, the concentration of silicon, iron, and aluminum is higher.

Studies of trace elements in plants, soils, and unconsolidated soil-forming rocks of the tundra landscapes of the Kola Peninsula (Dobrovolsky 1963), Central Siberia (Vasilevskaya 1980), and Alaska (Shacklette 1962) have shown that various systematic groups of plants take up selectively most of the heavy metals; as distinct, titanium, zirconium, yttrium, and gallium are poorly absorbed. Shown in Fig. 16 are the coefficients of biological absorption (K_b) of trace elements as taken up by widespread tundral plants thriving on the flatlands of the Khibini Mountains (the Kola Peninsula). One will observe that the K_b's for lead, zinc, tin, nickel, and copper are an order of magnitude higher above those for zirconium, titanium, and vanadium. The selective accumulation of metal by plants has profitably been made use of in the prospecting for copper-nickel ore deposits (Chapman *et al.* 1960; Dobrovolsky 1964).

Rockfoils (representatives of the genus *Saxifraga*) and mosses (bryophytes) are especially sensitive to metal concentrational changes. Shacklette (1958, 1962) has carried out detailed biogeochemical studies of the tundra landscapes of Alaska and established that the bryophytes are capable of sustaining higher concentrations of some metals as compared to vascular plants. Some moss species serve as indicators for ore deposits with elevated copper content.

Under the conditions of the free drainage commonly encountered in slopes and the positive elements of a relief, acidic brown tundral soils are formed. Characteristic of such soils is the accumulation of poorly degraded plant remains and the buildup of a differentiated peat horizon. Below this horizon, the soil profile differentiation is indistinct. In the thin indistinct humic horizon underlying the peat horizon, the humus content is 1-2.5%. Compositionally, predominant in the humus are readily soluble fulvic acids; the soil pH in the upper horizons is about 5. Acid soil solutions facilitate the aqueous migration of metals which are preferably transported as organic complexes.

On the territory of lowland plains with an impeded drainage in the lower part of the soil profile, the deficiency of oxygen is a common condition. This is favorable to the formation of gley tundra soils with a gray gleyic horizon.

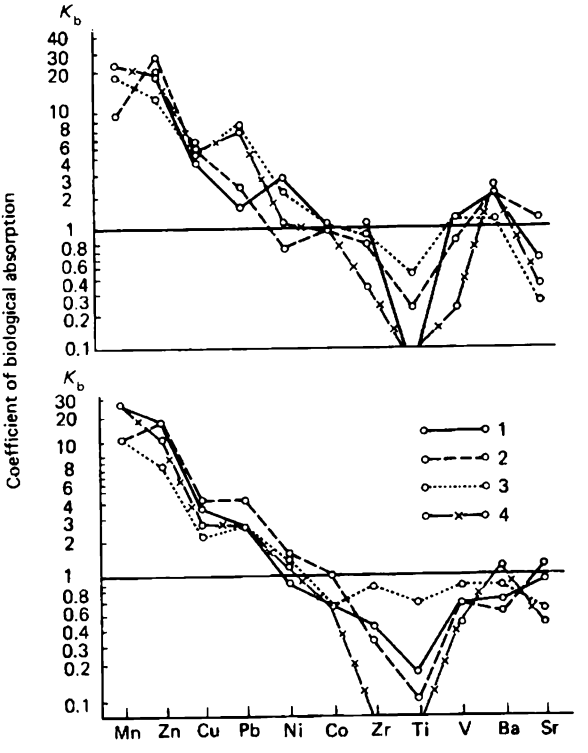


Fig.16. Biological uptake of metals by the vegetation of Karelian spruce forests growing on diabase outcrops (top picture) and gneiss outcrops (bottom picture)
1—spruce needles; *2*—spruce bark; *3*—hypnaceous mosses; *4*—leaves and twigs of blueberry (*Vaccinium uliginosum*)

This horizon starts immediately from beneath the humic peat horizon and goes down to the permafrost surface. Occasionally, one may observe a thin horizon, sandwiched between the humic horizon and the gleyed part of soil profile and exhibiting an alternation of gray and rusty spot-like inclusions which provide evidence for the precipitation of gels of Fe(III) oxides and mineral organics.

The vegetation biomass of tundral ecogeosystems tends to gradually increase from 4-7 ton/ha to 28-29 ton/ha on going over from the moss-lichen tundra to low-bush tundra. In the transitional subzone of forest tundra, the biomass is in excess of 100 tons per hectare. The mass of the organic matter confined to the soil surface and composed of peaty plant remains reaches 80-90 tons

Table 8.4. Heavy Metals and Other Trace Elements Involved in the Biological Cycle of Low-Bush Moss Tundra

Element	Elemental uptake, kg/m² per year
Fe	18.800
Mn	22.600
Ti	3.150
Zn	2.820
Cu	0.710
Zr	0.700
Ni	0.188
Cr	0.165
V	0.141
Pb	0.116
Y	0.070
Co	0.047
Mo	0.043
Sn	0.024
Ga	0.005
Cd	0.003
Average ash content of vegetation mass, %	2.0
Total uptake of ash elements by vegetation, ton/km² per year	4.5

per hectare by dry weight. In the northern tundra, the vegetation biomass accounts for over 50% of the total of vegetable biomass and dead organic matter. Southwards, this percentage tends to diminish, and in the low-bush tundra, the biomass is smaller than the biomass of plant remains. A typical feature of the tundra vegetation is the strong dominance of the mass of underground plant organs (70-80%) over the mass of aboveground parts (30-20%).

Rodin and Basilevich (1965) have reported the following average data on mass distribution in the most widespread type of tundra vegetation, the low-bush moss tundra (in ton/km²): biomass, 2800; dead organic matter, 8300; annual growth, 2038; annual litter production, 2027. Annually, about 5 tons of nitrogen per square kilometer becomes involved in the biological cycle.

Data on the average concentrations of trace elements in the vegetation of various natural zones are not as yet available. To circumvent this drawback, one must use the average values for the biomass of vegetative organs of the

World's land vegetation (see Chapter 2), with allowance made for the average ash content of vegetation in each zone. The average content of ash elements in the World's land vegetation is about 5% by dry weight. In the tundra vegetation, the ash content is smaller, about 2% of dry biomass. It is to be emphasized that the case in point is the "true ash content", that is, the quantity of elements making part of the tissue composition rather than the mechanical admixture of mineral dust particles whose percentage in the plants of certain natural zones may happen to be in excess of the "true ash content".

Given the average "true ash content" of 2% and the above data about the annual growth mass, one comes to an estimate of 4.7 tons per square kilometer of chemical elements (with the exception of nitrogen) in the vegetation of low-bush moss tundra annually involved in the biological cycle. Based on this value and the average concentrations of trace elements in the annual growth of land vegetation (see Table 1.5), one can calculate tentatively the masses of some elements entrained in the biological cycle. The relevant data are summarized in Table 8.4. The mass per unit area of chemical elements involved in the biological cycles of tundral ecogeosystem is not proportional to the uptake of these elements by vegetation. Presumably, some elements (for example, zinc and copper) are taken up selectively, whereas others are absorbed passively, depending on their level in the environment (for example, titanium, zirconium, vanadium, and yttrium).

9 Biogeochemistry of Boreal and Subboreal Forests

The forest landscapes of cold and temperate climates are quite widespread on the Earth's land. They occupy an extended zone in the northern part of the Northern Hemisphere continents. The overall area of forest landscapes in this zone is 16782 thousand square kilometers, or 11.2% of the total of World's land territory.

9.1. Biological Cycle of Elements in Forest Communities

The vegetation of boreal and subboreal forests concentrates a significant part of living matter of the planet, about $700 \cdot 10^6$ tons of dry weight. The biomass per unit area of forests of different type varies from $10 \cdot 10^3$ to $30 \cdot 10^3$ ton/km^2, reaching as much as $40 \cdot 10^3$ ton/km^2 in eastern European oak forests. The annual growth (productivity) in coniferous northern taiga forests is about 450 ton/km^2, in coniferous and mixed forests of southern taiga, 800 ton/km^2 or higher, and in broad-leaved subboreal forests, up to 900 ton/km^2.

The forest ecogeosystems of interest share a common biogeochemical feature — the prolonged retention of taken up chemical elements in the living matter. For this reason, the overall biomass per unit area of forest phytocenosis is 20 to 50 times higher than the annual growth. The slow mass transport of elements within the biological cycle of forest ecogeosystem is to a certain degree due to the fact that most of the biomass (about 80%) is found above the ground, and the died-off parts of plants fall onto the soil surface to form a thick forest litter.

The microbiological activity in forest soils is quite intense; fungi, along with bacteria and actinomycetes, play a specifically important role owing to their active involvement in the degradation of carbohydrates, the major components of forest vegetation litter. Because of the lengthy cold season, inhibitory to microbiological activity, the deciduous parts of plants never undergo a complete degradation. With the increasing duration of cold winter season from south to north, the mass of half-decayed plant remains increases accordingly from 1500 tons of dry organic matter per square kilometer in broad-leaved forests to 8000-8500 ton/km^2 in northern taiga forests.

Bogs constitute an inalienable part of the World's land forest zone. In certain regions, for example, in the territory of the vast Zapadno-Sibirskaya Ravnina, bog landscapes and water-logged localities account for over one third of the total area. The biogeochemical situation that exists in the bog landscape is very specific. The slow biological cycle of chemical elements typical of all boreal forest ecogeosystems is still more pronounced in the ecogeosystem of bogs. In sphagnous bogs, as the most widespread type of bog phytocenosis, the annual production accounts for about 10% of living biomass and fractions of a percent of the mass of dead organic matter of peat accumulations.

In the northern variants of forest phytocenosis, the percentage of certain chemical elements in the dead organic matter of forest litter is higher than that of the living biomass. In mixed and deciduous forests, the number of chemical elements in the litter is smaller than that in the biomass, although the absolute element masses in the litter are quite large. Thus, along with a significant amount of elements present in the living vegetable mass, a large reserve of elements is stored in the organic matter of forest litter. The retarded mass-exchange cycle in the photosynthesis-degradation process of organic matter sets a limit to the rate of elemental mass migration in the soil-vegetation system. The retardation of the biological cycle of elements increases with the boreal tendency of the environment.

Generalized data on the distribution and dynamics of the masses of living matter and nitrogen in the typical phytocenoses of forest zone of the Northern Hemisphere are summarized in Table 9.1.

The sum total of ash elements ("true ash content") is appreciably different in different organs of a tree. As follows from the data by Rodin and Bazilevich (1965), the ash content of the needles and twigs of conifers from boreal forests is nearly 10 times the ash content of trunk wood. For this reason the ash content of the total biomass of forest vegetation and of the mass of annual production and sheddings are also different. The average of the total of ash elements in the annual production and sheddings of the northern taiga coniferous forests is close to 1.7% (by dry weight), and that for the coniferous and parvifoliate subboreal forests, about 2%. With allowance made for the above ash content and for the annual mass production (Table 9.1), 7.6 tons per square kilometer is annually involved in the biological cycle in the spruce forests of the northern taiga, and 17 tons in the southward, more productive spruce and parvifoliate (needle leaf) forests.

The sum total of ash elements in the production of broad-leaved forests commonly amounts to 2.5 to 4.0% (by dry weight), the acceptable mean value being 3.5%. The mass of ash elements involved in the biological cycle in the most productive phytocenoses of broad-leaved subboreal forests (oak forests) is 31.5 tons per square kilometer. Regrettably, no average concentrations for trace elements in the annual growth and sheddings of zonal vegetable types

Table 9.1. Distribution and Dynamics of the Masses of Living Matter and Nitrogen in the Widespread Types of Vegetation of the Forest Zone of Russia (according to the data of Rodin and Bazilevich (1965); all values in ton/km^2)

Biological cycle components	Spruce forest of northern taiga	Spruce forest of southern taiga	Oak forest	Sphagnous bog of southern taiga
Biomass	10000	33000	40000	3700
Nitrogen	35	72	115	22.9
Annual production	450	850	900	340
Annual uptake of nitrogen	5.8	4.1	9.5	4.0
Litter production	350	550	650	250
Annual return of nitrogen	4.8	3.5	5.7	2.5
Dead organic matter (peat, forest litter)	3000	3500	1500	10000

are as yet available. For this reason, the only way to an estimation of elemental masses involved in the biological cycle is to make use of approximate average concentrations in the annual poduction of the World's land vegetation. The relevant data have been listed in Table 1.5. The zonal biogeochemical specificity of mass migration is taken account of through applying an appropriate correction for ash content for a particular type of vegetation, which permits estimating the order of magnitude for migratory masses of most elements. Certainly, one must be aware of the fact that this method of calculation levels off the biogeochemical specificity of individual elements. For example, strontium is accumulated by the vegetation of taiga forests at a level below the average for the World's land vegetation, whereas the exact opposite holds for manganese. With due regard for the said allowance, the tentative estimate of the masses of heavy metals and trace elements involved in the biological cycle of forest ecogeosystems provides the possibility for a comparison with migratory masses in other natural zones. The calculated results are presented in Table 9.2. To calculate the masses of elements in the annual production of sphagnous bogs, the average elemental concentrations as reported for the raised bog peat (see Table 4.5) have been used.

The data in Table 9.2 provide a general characterization for the distribution and migration of masses in the vegetational zone of boreal and subboreal forests.

Table 9.2. Masses of Trace Elements Involved in the Biological Cycle of Widespread Landscapes in the Forest Zone

	Coniferous forests of northern taiga	Coniferous and parvifoliate subboreal forests	Broad-leaved subboreal forests	Sphagnous forest bogs
Average ash content, %	1.7	2.0	3.5	2.5
Total uptake of ash elements, ton/km^2 per year	7.6	17.0	31.5	8.5
Elements and their turnover, kg/km^2 per year				
Fe	30.4	68.0	126.0	150.0
Mn	36.4	81.6	151.2	7.51
Sr	5.32	11.9	22.1	6.80
Ti	4.94	11.1	20.5	40.12
Zn	4.56	10.2	18.9	6.26
Cu	1.22	2.72	5.04	1.22
Zr	1.14	2.55	4.72	1.43
Ni	0.30	0.68	1.26	1.36
Cr	0.26	0.59	1.10	1.09
V	0.23	0.51	0.94	1.02
Pb	0.19	0.42	0.79	1.20
Co	0.07	0.17	0.31	0.23
Mo	0.07	0.15	0.28	0.10
Sn	0.04	0.08	0.16	—
Ga	0.01	0.02	0.03	0.4
Cd	0.005	0.012	0.022	—

Each given region and each particular type of ecogeosystem have their intrinsic features. Let us discuss, by way of example, the structure and mass-exchange dynamics in the spruce forests of Karelia.

The spruce forests, widespread south of 63° N, take more than half of territory of the said region. Along with the dominant species, the spruce (*Picea excelsa*), minor species present are the birch (*Betula verrucosa, B. pubescens*), aspen (*Populus tremula*), and alder (*Alnus incana*). The moss-and-low-bush layer is represented by the bilberry-bush (*Vaccinium myrtillus*), hypnic mosses, separate specimens of cowberry (*Vaccinium uliginosum*) and flowering plants.

Table 9.3. Biomass and Ash Element Distribution in Spruce Forests of Karelia (Based on the Data by Kazimirov *et al.* 1974)

Biomass components	Biomass	Annual growth	Litter production
Woody vegetation, ton/km^2	400-10000	400-900	200-550
of this:			
needles, %	10-15	36-38	56-60
twigs, %	12-17	8-9	8-9
trunks, %	50-60	41-43	22-25
roots, %	17-19	12-13	9-10
Moss and low-bush vegetation, ton/km^2	80-350	20-60	20-60
	Total (100%) of ash elements		
Woody vegetation, of this:			
needles, %	40-50	79-80	76-81
twigs, %	13-18	4-5	2-3
trunks, %	19-33	10-11	4
roots, %	12-14	4-5	2-3
Moss and low-bush vegetation, %	3-8	5-9	7-10

The biomass of a spruce forest aged 100-150 years reaches $10 \cdot 10^3$ tons per square kilometer (by dry weight); not infrequently, it may happen to be smaller in value.

As will be observed in Table 9.3, most of the spruce forest biomass is accounted for by trees, the predominant part of their mass being confined to the trunk. In the vegetable weight gain and, especially, in the sheddings, the relative contribution due to the conifer needles and to the moss-and-low-bush layer becomes more important. In living matter, the mass of moss-and-bush vegetation makes up to 2-3% of the tree biomass, whereas in dead matter (sheddings), it is 10%.

The ash element distribution in the living vegetable matter is distinct from that in the dead matter. About half of the total of ash elements contained in the biomass is confined to the deciduous tree organs, whereas for the sheddings, most ash elements are found in the needles. About 80% of ash elements (with respect to their content in the sheddings) is supplied from conifers to the soil

Table 9.4. The Mass Balance for the Total of Ash Elements in the Biological Cycle of Coniferous Forests in Karelia

Phytocenosis component and its biomass ash content	Annual growth, ton/km^2 year^{-1}		Annual shedding, ton/km^2 year^{-1}	
	dry organic matter	ash elements, total of	dry organic matter	ash elements, total of
Moss-and-shrub vegetation, 1.7%	20-60	0.34-1.02	20-60	0.34-1.02
Conifer needles, 1.7%	144-342	2.45-5.81	112-330	1.90-5.61
Conifer bark, 1.3%	20-54	0.26-0.70	10-30	0.13-0.39

in the shed needles, whereas their supply in the deciduous organs of moss-and-bush vegetation is a mere 10%. Shedding is not the only route enabling the living vegetable tissue to be relieved of the ash elements. Some of these are delivered to the outer bark to be retained therein for a longer period of time. Therefore, in estimating the elemental mass transport in forest phytocenoses, one must take into account, along with the return of elements to the soil, the retention of elements in the bark. The involvement of ash elements in the biological cycle of spruce forests is illustrated by the data in Table 9.4. The sum total of ash elements retained in the outer bark (0.26-0.70 ton/km^2) is commensurate with that supplied to the soil in the bush vegetation sheddings.

The quantitative characterization of major ash elements involved in the biological cycle of spruce forest phytocenosis is presented in Table 9.5 (after Kazimirov *et al.*, 1974). The results in Table 9.5 show that for calcium, potassium, and silicon, the turnover in the biological cycle is within a range of 1 to 3 ton/km^2 per year. The turnovers for magnesium, phosphorus, manganese, sulfur, and aluminum are hundreds and for iron and sodium, tens of kilograms per square kilometer per year.

The trace element concentrations in the spruce and the bilberry as major plant species of spruce forests are summarized in Table 9.6. In examining the presented evidence, one will observe the following.

First a wide variation of concentration in the samples is to be noted. The coefficient of variation is seldom smaller than 60% and is often in excess of 100%. Second, despite the wide concentrational variation, one will observe a trend in the biogeochemical specialization of plants and their organs.

The concentration of strontium, barium, and titanium in the spruce bark is relatively higher than in the needles, while the latter are richer in nickel and

Table 9.5. Mass Balance of Ash Elements in the Phytocenosis of Spruce Forests in Karelia

Element	Elemental content, ton/km², in:		
	phytocenosis biomass	annual production	annual sheddings
Ca	20.5 (15.0-26.0)	3.20 (2.0-4.5)	2.7 (1.5-4.0)
K	11.0 (5.0-17.0)	1.55 (0.7-2.4)	1.3 (0.6-2.0)
Si	5.2 (4.0-6.5)	1.45 (1.0-1.9)	1.35 (0.9-1.8)
Mg	3.2 (2.5-4.0)	0.55 (0.4-0.7)	0.45 (0.3-0.6)
P	3.0 (1.5-4.5)	0.40 (0.2-0.6)	0.30 (0.1-0.5)
Mn	2.0 (1.5-2.5)	0.33 (0.22-0.45)	0.29 (0.19-0.39)
S	0.80 (0.6-1.0)	0.16 (0.12-0.21)	0.15 (0.12-0.19)
Al	0.85 (0.5-1.0)	0.15 (0.1-0.2)	0.12 (0.07-0.18)
Fe	0.70 (0.35-0.80)	0.08 (0.05-0.12)	0.08 (0.04-0.11)
Na	0.15 (0.05-0.25)	0.03 (0.01-0.05)	0.02 (0.01-0.03)
Total	42.90 (30.0-60.0)	7.9 (4.7-10.7)	6.76 (4.0-9.0)

Note: Values presented are the arithmetic mean; the range of variation is given in parentheses.

zinc. The concentration of certain metals is higher in the bilberry roots, than in the stem. Third, the effect of zonal and local factors is notable at elemental concentration level. The concentration of strontium in the needles and the bark of the spruce as well as in the bilberry is appreciably lower than the average concentration of this element in the sheddings of the World's land vegetation. This should be attributed to the effect of zonal factors on the active release of this element. At the same time, the elevated concentration of lead and zinc reflects the specificity of the bedrock characterized by a dispersed sulfide mineralization in a particular region.

The bedrock composition exerts influence on the concentration of individual metals. We have shown in our studies that the needles and the bark of spruces grown on territories adjacent to diabases are higher in nickel and vanadium as compared to those grown on granite gneiss outcrops. However, such concentrational differences are rather small and often pass unnoticed because of the effect by other factors. In particular, in territories with a diabase bedding underlying shallow detrital deposits, the elevated concentration of nickel and vanadium was detected in spruce trees only, whereas no trace of these elements was found in the leaves and the stems of small shrubs. Presumably, this might

Table 9.6. The Concentration of Trace Elements in Major Plant Species of Spruce Forests in Karelia

Element	Spruce (*Picea excelsa*)				Bilberry (*Vaccinium myrtillus*)			
	needles		bark		aerial parts		roots	
	M	*V*, %	*M*	*V*, %	*M*	*V*, %	*M*	*V*, %
Zn	1250	98	1188	90	751	190	1515	161
Ba	390	65	456	76	465	71	578	22
Ti	102	100	170	330	113	130	86	110
Cu	86	86	88	60	107	90	124	51
Pb	64	60	62	130	84	77	111	85
Sr	43	60	73	88	35	85	33	84
Zr	38	36	33	61	20	27	28	48
Cr	28	51	26	42	28	37	34	56
Ni	23	100	17	120	19	71	25	
V	16	42	23	55	19	26	14	41
Co	12	80	13	61	13	70	14	70

Note: *M* is the arithmetic mean; *V* is the coefficient of variation; all values, except those of *V*, are in μg/g (ash weight basis)

be due to the essentially shallow root system of small shrubs as distinct from the deep-penetrating spruce tree roots. Experimental works as carried out in a large number of regions of the forest zone have shown that the glacial deposits cover a few meter thick levels off the concentrational content of trace elements over vast territories (Dobrovolsky, 1964).

The elucidation of the biological cycle organization and the establishment of the concentrational levels of trace elements in the renewable parts of plants have provided the possibility of estimating to a first approximation, the biogeochemical migration of these elements. The relevant data are presented in Table 9.7. As has been ascertained, the arborous vegetation confined to an area of 1 km^2 of spruce forest absorbs annually from the soil a few kilograms of zinc and barium, hundreds of grams of copper, lead, strontium, zirconium, tens of grams of nickel, vanadium, and cobalt. The metal mass uptaken by low-bush vegetation is smaller by an order of magnitude. Simultaneously, nearly the same amount of metals is released from the living biomass of spruce forest.

Of great interest has been the estimation of a relative uptake of trace elements by forest vegetation. The measurements of coefficients of biological absorption (K_b) have shown that, independent of the composition of crystalline bedrock

Table 9.7. The Biological Turnover of Trace Elements in the Phytocenosis of a Spruce Forest

Vegetation components involved	Elemental turnover, kg/km² per year						
	Zn	Cu	Pb	Ni	Co	Ba	Sr
Needles:							
newly grown	3.0-7.0	0.2-0.5	0.2-0.4	0.05-0.10	0.03-0.10	1.0-5.0	0.1-0.2
lost in shedding	2.5-7.0	0.2-0.5	0.1-0.3	0.04-0.10	0.02-0.06	0.8-2.0	0.08-0.2
Bark:							
newly grown	0.4-0.8	0.03-0.06	0.02-0.04	0.01-0.02	0.003-0.004	0.2-0.4	0.02-0.04
lost in shedding	0.2-0.5	0.01-0.04	0.01-0.02	0.03-0.01	0.002-0.004	0.07-0.2	0.01-0.03
Shrub vegetation:							
newly grown	0.3-0.8	0.03-0.1	0.03-0.08	0.008-0.02	0.004-0.01	0.2-0.5	0.02-0.05
lost in shedding	0.3-0.8	0.03-0.1	0.03-0.08	0.008-0.02	0.004-0.01	0.2-0.5	0.02-0.05
Total uptake by vegetation	3.7-8.6	0.26-0.66	0.25-0.52	0.068-0.14	0.037-0.11	1.4-5.9	0.14-0.29
Total shedding	3.0-8.3	0.24-0.64	0.14-0.40	0.051-0.13	0.026-0.074	1.07-2.7	0.11-0.28
Accumulated in tree bark	0.2-0.3	0.02	0.01-0.02	0.007-0.01	0.001	0.13-0.2	0.01

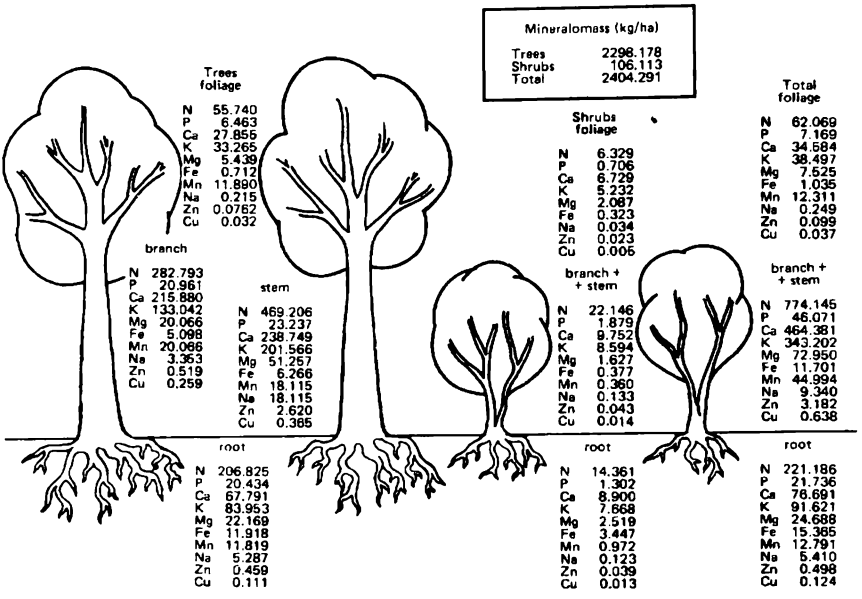


Fig. 17. Mass distribution of chemical elements in the phytocenosis of an oak forest in the northern Hungary (Jakics 1985)

and the depth of detrital deposits, the uptake rate for each element is maintained at a steady level. The intense uptake is typical of zinc, manganese, copper, and lead, with their K_b's falling into a wide range of 2 to 30. Poorly absorbed are nickel and cobalt, for which the K_b is slightly higher above 1. Very reluctant to be taken up are titanium, zirconium, and vanadium, with their K_b smaller than 1.

The intensity of involvement of trace elements in a biological cycle is independent of their elemental concentration in rocks. By way of example, presented in Fig. 17 are the K_b's of trace elements measured for the spruce (needles and bark), low bush, and hypnous moss. One will observe that the curves follow a similar pattern independent of the composition of the bedrock — diabasic or gneissic — underlying the forest phytocenoses. Simultaneously, various plants absorb the same elements at a different rate. In particular, mosses are better accumulators of poorly absorbable elements (titanium, zirconium, vanadium) than trees and small shrubs.

The shed mass of a spruce forest aged 150 years is 400-550 tons per square kilometer. Hypothetically, if the total of sheddings had been preserved, about 50 000 tons of plant remains per square kilometer would have been stored within a period of 100 years. However, the litter mass in all of the explored forests is merely $2\text{-}3 \cdot 10^3$ tons per square kilometer, which makes up a few

percent of the above mentioned hypothetical dead organic matter. There are substantial masses of trace metals in the forest litter: zinc, lead, and copper, measured by thousands of kilograms per square kilometer; hundreds of kilograms of nickel; tens of kilograms of cobalt and tin. Exposed to microbiological processes, the dead organic matter undergoes degradation, and the trace elements become mobilized, most of them reentering the biological cycle.

Bogs are widespread in the Karelian territory. For one thing, the biogeochemistry of silvan and paludal phytocenoses is strikingly different. The dry biomass of the region that has been explored was 700 to 1100 tons per square kilometer (without regard for singly growing trees), which is almost ten times smaller than the forest biomass.

The annual growth of moor vegetation is about 350 ton/km^2, which is twice as small as that of forest vegetation. In the bog, the degradation of dead organic matter proceeds at a much slower rate as in the forest. The mass of peat accumulated within a period of 100 years accounts for some 20% of the organic material formed in bog landscapes. This is nearly ten times higher above the relative mass of dead organic matter preserved in forests.

On degradation of organic matter, iron and trace elements accumulate in stagnant waters. Consequently, the trace metals become taken up in larger concentrations by the local vegetation. For this reason, in the paludal phytocenoses, despite the smaller mass of sheddings as compared to that in forests, quite commensurate and, occasionally, even larger masses of trace metals are involved in the biological cycle. In an area of 1 km^2, the annual uptake by moor vegetation of zinc, barium, lead, and titanium amounts to several kilograms; of copper, zirconium, chromium, nickel, and vanadium, hundreds of grams; of cobalt, tens of grams.

The bog and forest landscapes grade into each other with a varied degree of distinction through transitional zones which may look like moderately wet swamps grown with trees and shrubs, or like water-logged forests. The bog development manifests itself in a decreased mass of phytocenosis, in the predominance of moss vegetation in the biological cycle, and in higher concentrational levels of iron and certain trace elements.

Southwardly from the northern border of boreal forests, the natural humidity of the environment gradually decreases simultaneously with the shortening of the cold winter season which inhibits biogeochemical processes. Accordingly, the floristic composition of silvan phytocenoses and the geochemical specialization of dominant plants also is altered. The coniferous forests grade into mixed ones and then into deciduous forests. The small shrubs and mosses become replaced by herbaceous vegetation which is turning into a predominant type. As the activity of biogeochemical processes intensifies, the annual production of biomass also increases and, accordingly, the mass of shed material; simultaneously, the mass of dead organic matter tends to decrease. Concurrently, changes occur

in the chemical composition of plants and in the proportion of chemical elements involved in the biological cycle.

The broad-leaved forests thrive in regions with a well-balanced precipitation-to-evapotranspiration ratio and with the coefficient of humidity from 0.75 to 1.20 (see Section 6.1). The southern periphery of the vast belt of Eurasian boreal and subboreal forests is represented by oak forests. Among the silvan communities of the zone in question, these exhibit both the largest biomass and annual production. Simultaneously, the mass of the surficial dead organic matter is two to three times less than that of coniferous forests. In water-logged forest soils, the degradation of plant remains proceeds at a slower rate, with the resultant increase in forest litter mass.

Alterations in the chemical composition of vegetation are as follows. The content of nitrogen in the fallen leaves as a major shedding component is about twice as large as that in the needles of conifers. The sum total of ash elements in the leaves accounts for 3.5 to 5% (average about 4%) on a dry weight basis. Accordingly, the concentrations of calcium are increased (from 0.5 to 4.0%), potassium (from 0.15 to 2.0%), and silicon (typically, with a wide variation). According to the data by Rodin and Bazilevich (1965), the elements are arranged in their order of uptake decreasing as $C > N > K > Si \cong Mg \cong P \cong S > Al \cong Fe \cong Mn$.

The amount of nitrogen in the biomass of oak forests reaches 90-120 tons per square kilometer; for comparison, the sum total of ash elements is largely in excess of nitrogen and amounts to 200-300 tons per square kilometer, or, reportedly, even higher. The annual growth contains 8-10 tons of nitrogen and 20-25 tons of ash elements per square kilometer. An essential point is that the green leaves store 70-80% of the mass of uptaken elements, and the fallen leaves, 80-90% of the mass of elements eliminated from the biological cycle. Nitrogen as returned in the shedding products amounts to 4-7 tons, and the ash elements, to 18-20 tons per square kilometer.

A team of Hungarian researchers headed by P. Jakucs (1985) has studied, under the "Man and the Biosphere" program, the distribution and mass-exchange dynamics of chemical elements in the oak forest reserve in the vicinity of Eger (Northern Hungary). The principal timber species is *Quercus petraea* accounting for 78% of the wood mass; *Quercus cerris* accounts for 22%. The shrubs are chiefly represented by *Acer campestre* and *Cornus mas*, and the grass, by the genera *Carex, Dactylis,* and *Poa*.

The mass of trees is 24103.4; of shrubs, 654.2; of herbaceous vegetation, 61.8; of mosses, 4.8 tons per square kilometer. The trees are major contributors to the annual production, they synthesize 1078.4 tons of organic matter per square kilometer per year; the respective value for shrubs is 169.8, for grasses, 41.3, and for mosses, 0.16. The distribution of chemical elements in biomass and annual growth is shown in Fig.18 and summarized in Table 9.8. Among

Table 9.8. Biological Turnover of Trace Elements in the Phytocenosis of an Oak Forest in North Hungary (after Jakucs *et al.* 1985)

Element	Element content in biomass, kg/km²			Total uptake by vegetation, kg/km² per year		
	in leaves	in twigs, in stem	in roots	trees	shrubs	total
N	6206.9	77414.5	22118.6	10338.7	1448.5	11782.2
P	716.9	4607.1	2173.6	1190.5	157.9	1348.4
Ca	3458.4	46438.1	7669.1	6086.3	1347.9	7434.2
K	3849.7	34320.2	9162.1	7979.6	1228.0	9207.6
Mg	752.6	7295.0	2468.8	1189.1	390.5	1579.6
Fe	103.5	1170.1	1536.5	153.7	130.9	284.6
Mn	1231.1	4499.4	1279.1	1912.4	85.5	1997.9
Na	24.9	934.0	541.0	100.8	14.3	115.1
Zn	9.9	318.2	49.8	28.0	3.6	32.6
Cu	3.7	63.8	12.4	6.3	1.0	7.3

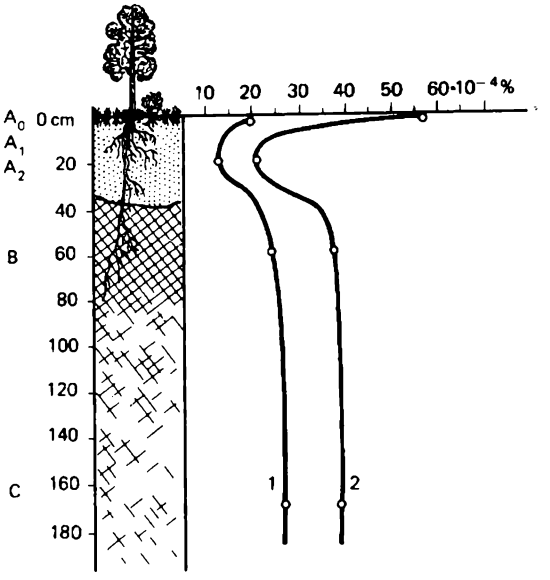


Fig. 18. Distribution of vanadium (*1*) and copper (*2*) down the podzolic soil profile (extraction with 1 N HCl)

the ash elements, the most abundant in biomass is calcium accumulated not only in leaves, but also in trunk wood and in twigs. Potassium is dominant in annual growth. The masses of heavy metals involved in the biological cycle are in a rough correspondence with their respective averages for the oak forest communities of subboreal climate. An exception to the rule is manganese, with its inordinately large masses in both mass exchange and annual growth. Possibly, this phenomenon should be attributed to local landscape-geochemical specificities.

It may be of interest to compare the masses of migratory elements in the biological cycle of the forest under study with the masses supplied from the atmosphere by precipitation. According to the available data, the atmospheric supply of precipitated metals is (in kg/km^2 per year): for calcium, 1474; magnesium, 180; potassium, 423; sodium, 139; phosphorus, 114; iron, 7; and zinc, 14. The masses of major atmospheric elements fall into a range of 20% (calcium) to 4.5% (potassium) relative to the respective masses involved in the biological cycle. The mass of atmospheric iron accounts for a mere 2.5%. Simultaneously, for some heavy metals (for example, zinc), the atmospherically supplied mass is commensurate with the mass involved in the biological cycle.

9.2. Biogeochemical Characterization of the Soils of Boreal Forest Zone

The forest landscape soils, however diverse they might appear, share a number of common features originating in the similarity of processes occurring therein. The retarded biological cycle provides for the buildup on the top soil of a covering layer of partly decomposed deciduous parts of plants, the forest litter (A_0 horizon). The predominance of precipitation over evaporation and the availability of easily soluble humic acids (produced through decomposition of the plant remains by microorganisms, and, particularly, by fungi) is favorable to the formation of permeable, readily washed-out soils.

Characteristic of the forest landscape soils of all types is the accumulation of nutritional elements in the forest litter overlying the elluvial soil horizon. Down the soil profile, the concentration of nutritional trace elements increases gradually till the soil-forming rock is reached. In certain soils, a horizon overlying the elluvial horizon and containing some elements in slightly elevated concentration may occasionally form. In the illuvial taigal podzols, this is due to the precipitation of organic compounds and hydrated iron oxides capable of retaining heavy metals and their congeneric trace elements. In acid brown and sward-podzolic soils of deciduous forests, the effect of lessivation (also known as illimerization) occurs manifested as the washing-out of finely-dispersed particles from the uppermost part of the soil profile and their deposition in the medium part. Cotransported with the dispersed particles are elements adsorbed thereon.

Two groups of elements as specified by their distribution along the soil profile are distinguished. The representatives of the first group are actively absorbed by forest vegetation and, at the same time, are relatively tightly held in the dead organic matter. Their concentration in A_0 horizon is higher than that in the soil-forming rock. For the second group representatives, the concentration in A_0 horizon, although elevated in comparison to the elluvial horizon, fails nevertheless to reach the level of soil-forming rock. Included in the first group are manganese, zinc, copper, lead, nickel; typical of the second group are titanium, zirconium, vanadium, and chromium. Typical curves for the distribution of heavy metals along the soil profile of boreal forests are shown in Fig. 19.

The differentiation of trace elements along the soil profile should be regarded as the final result in the redistribution of their various forms. In these, the highest diversity is achieved precisely in the soil owing to a vast varicty of biogeochemical processes involved. To the soil forms as originated from the initial soil-forming rocks are added biogenic forms, those constituting the dead organs and higher plant metabolites and those produced in the course of biotic activity of microorganisms.

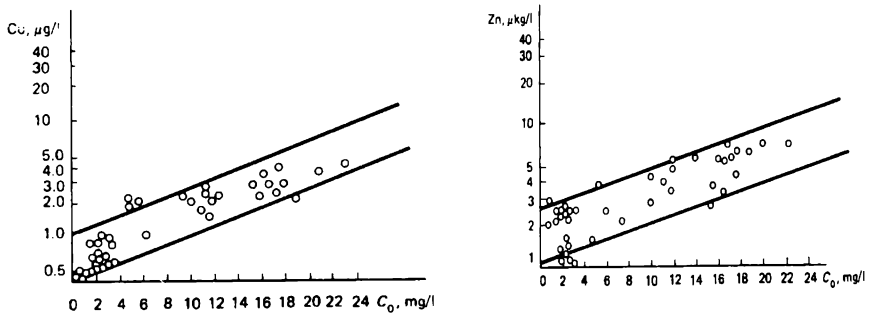


Fig. 19. Concentration of copper (left) and zinc (right) as a function of the organic soluble matter concentration in ultrafresh permafrost taiga landscapes of the East Siberia (Nikitina 1973)

Various forms differ among themselves in their ability to migrate and redistribute along the soil profile. The elements, contained in clastic minerals, are practically immobile. The elements bound to finely-dispersed clay minerals are either cotransported with the latter, or are involved in sorption-desorption processes. Part of the elements are found in concretions and also in very thin coating films of hydrated iron oxides; some elements make part of specifically edaphic organic compounds.

The determination of all forms of trace elements is quite an arduous task. Nonetheless, the available data allow one to estimate, in an approximate manner, the proportion of major forms in certain soils.

In the landscape of mixed forests of the Srednerusskaya Vozvyshennost', the most widespread are derno-podzolic soils of loamy composition. The soil fraction sizing less than 1 μm contains most of the elements previously confined to the forest litter and later actively involved in the biological cycle. In this fraction, copper and molybdenum account for 60-70% of the total of either metal contained in the soil. The metals, poorly absorbable by plants, for example, chromium and vanadium, occur in finely-dispersed soil fraction in smaller amounts, about 20-30%.

The data in Table 9.9 as reported by Titova (1970) and Zhuravleva (1970) illustrate the concentrational variation of major forms of copper and cobalt within the profile of derno-podzolic soils in the Podmoskov'e. One will easily see that the soluble and exchange forms of metals are present in small amounts accounting merely for a few percent of the total metal content in the soil. The concentration of organometal compounds is relatively high in the upper profile rich in humic species, whereas it drops sharply in the mineral horizons. Copper

Table 9.9. Distribution of Copper and Cobalt in the Podzolic Soils of Podmoskov'e (Moscow Region, Russia)

Soil horizon	Metal content in soil, 10^{-4} %	% of the total metal content			
		soluble and exchange metal forms	metal forms bound with:		
			organic matter	hydrated iron oxides	mineral matter of soil
		Copper			
A_1	7.4	3.1	32.4	51.3	13.2
A_1/A_2	7.4	3.6	24.3	45.9	26.2
A_2	6.0	3.2	26.7	55.0	15.1
A_2/B	16.8	2.7	3.6	40.5	53.2
B_1	20.6	3.8	4.4	43.2	48.6
B_2	19.4	3.9	4.6	54.1	37.4
BC	19.8	3.6	4.5	47.0	48.5
		Cobalt			
A_1	5.5	4.2	12.7	30.9	52.2
A_2	4.5	3.7	13.3	24.4	58.6
B_1	5.8	not determined	3.4	34.5	62.1
C	5.3	not determined	3.8	34.0	62.8

is actively involved in the biological cycle in the Podmoskov'e landscapes; the involvement of cobalt is less pronounced. Accordingly, the content of copper is twice as large as that of less mobile cobalt. It is noteworthy that a large part of metals (in particular, of copper) become bound to iron hydroxides. This is typical not only of metals, but also of arsenic and a number of trace elements with variable valence.

The excess ground humidity is favorable to the formation of gley soils. Gley-podzolic soils with massive forest litter provide conditions for a low water-logging. In high water-logging, a peat horizon is formed in the top soil reaching into a sizeable depth in boggy soils. In the forest litter of podzols, the concentration of fulvic acids is two to three times that of humic acids; by contrast, humic acids are predominant in the peat horizon of boggy soils. This is reflected in a lower pH of aqueous extraction from the forest litter of podzols and in a more active migration of elements from them.

The concentration of many metals in peat-boggy soils is often higher than that in podzolic soils. In boggy soils, the relative concentration of elements bound with humic acids is also significantly higher. In Karelia, in the forest litter of podzols, most of mobile nickel forms are bound to humic acid, and those of copper, to free fulvic acids. Copper fulvates are easy to wash out, therefore their content in the soil profile below the humus horizon is greater than that of copper humates. The concentration of metals consisting of organometal compounds of a different type in peat-boggy soils compares with that in podzolic soils; however, the overall mass of metal organics in the boggy soils is appreciably higher.

In the southerly direction, the podzolic soils grade into sward-podzolic, and then into forest light-gray soils. Simultaneously, both the soil acidity and element migration tend to decrease.

9.3. Effect of Edaphic Biogeochemical Processes on the Aqueous Migration in the Zone of Boreal and Subboreal Forests

The elements, mobilized owing to the biogeochemical processes occurring in the soil, become involved in aqueous migration through surface and groundwater runoff. Typical of the surface waters of boreal landscapes are low mineralization and the availability of appreciable amounts of soluble organic compounds. This feature is particularly distinct in cryogenic taiga landscapes where the zone of active water exchange in the river valleys is confined to suprapermafrost waters and to ice-thaw strips.

The source for feeding the suprapermafrost ground waters is atmospheric precipitation. The precipitation, despite its low mineralization, contributes significantly to the chemical composition of natural waters in boreal landscapes. The concentration of trace elements in the ground waters of cryogenic taiga landscapes of the North Siberia is lower than their respective average concentration in the World's land river waters. In boreal landscapes, the concentration of trace metals in ground waters is merely several-fold higher than that in rain-fall waters (see Table 9.10). The higher trace metal concentration in solid precipitation in comparison to liquid precipitation may presumably be due to an elevated content of solid particulate matter in snow. In the belt of coniferous taiga forests within the 60°-70° N strip, the monthly precipitation sample was shown to contain: manganese, 12; lead, 4.4; copper, 4.0; and nickel, 3.0 μg/liter. In the southern part of the forest belt confined to 50°-60° N, the concentration tends to slightly increase: manganese, 20; lead, 6.0; copper, 5.0; and nickel, 3.5 μg/liter. The metal masses as estimated above

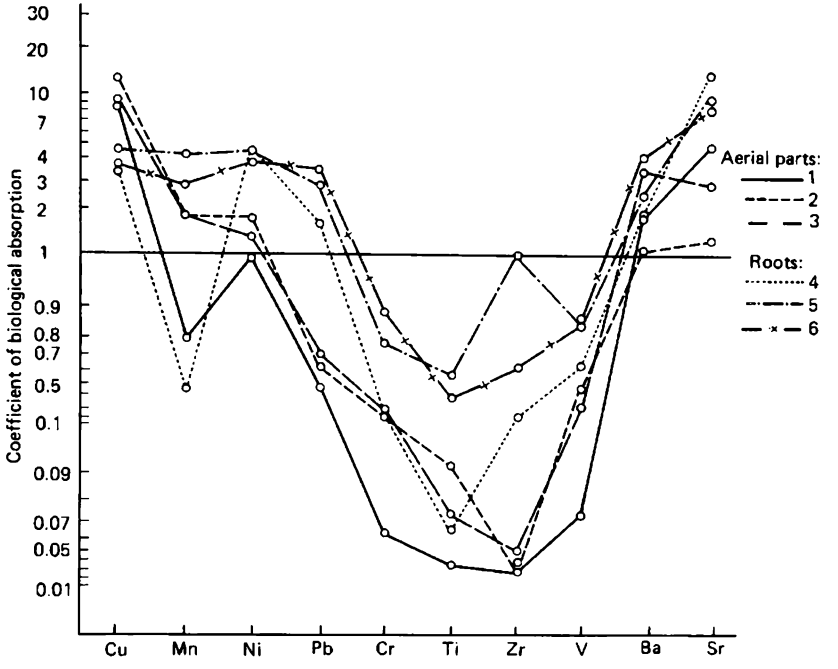


Fig. 20. Biological uptake of metals by typical steppe plants of the northern Sredne-Russkaya Vozvyshennost' (Savel'eva 1979)
Areal parts: *1*—clover; *2*—grasses; *3*—motley grasses
Roots: *4*—clover; *5*—grasses; *6*—motley grasses

play rather a modest role in the elemental mass exchange in the ecogeosystems of the southern forest belt; however, their contribution becomes more prominent in the northernmost regions, especially those subject to permafrost.

Nikitina (1973) has reported that in the cryogenic taiga landscapes of crystalline plateaus and highlands of the West Siberia, of frequent occurrence are ultrafresh waters. The mineralization of these amounts to 16-85 milligrams per liter, with the soluble organic species being in excess over the mineral. In the former, fulvic acids predominate which ligate copper, vanadium, nickel, cobalt, lead, yttrium, and beryllium to form organometal complexes. The concentration of the above-mentioned metals increases with the percentage of soluble organic matter (Fig. 20).

In the vast territory of the Eurasian forest zone in a southerly direction, the podzolic and cryogenic-taigal soils of coniferous forests grade into sward-podzolic soils of mixed forests to be replaced by the gray and brown soils of deciduous forests. Accordingly, the mineralization of surface waters increases,

Table 9.10. The Concentration of Heavy Metals in Atmospheric Precipitation and Ground Waters of Siberia (after Shvartsev 1978)

Element	Element concentration (μg/l)				
	tundra landscapes of the Sredne-Sibirskoye Ploskogor'e			taiga landscapes of the southern West Siberia	
	rain (3 samples analyzed)	snow (2 samples analyzed)	ground water (30 samples analyzed)	atmospheric precipitation (6 samples analyzed)	ground water (28 samples analyzed)
Mn	4.0	3.7	12.5	4.42	20.2
Zn	3.0	10.0	8.5	7.18	29.2
Cr	2.2	2.5	1.3	1.06	2.53
Cu	1.0	2.6	3.1	0.22	1.84
Ti	1.0	1.0	1.5	2.42	22.7
V	1.0	0.8	1.0	—	0.74
Pb	0.3	1.0	0.37	2.30	0.45
Ni	0.2	0.8	0.80	0.33	1.53

with a concommitant decrease in soluble organic acids. The noted systematic change reflects a general trend only which may be perturbed by the compositional variation of soil-forming rocks. The biogeochemical processes that occur in podzolic soils formed on sandy aqueoglacial and ancient alluvial deposits are favorable to a decreased mineralization of waters and to their relative enrichment in fulvic acids. Such a situation, in particular, is typical of the sandy lowlands of the Russkaya Ravnina, viz., Meshchera, Belorusskoye Poles'e, and other territories. As distinct, the spread of loamy soil covers makes an increase both in the pH and mineralization of natural waters. Nonetheless, the trend to a concentrational increase of trace elements in waters with decreasing landscape boreality is clearly visible in separate regions, in particular, Siberia (see Table 9.11). The concentrational rise is not the same for different elements, which makes the mineral proportion vary with increasing mineralization. For example, zinc is the most abundant element in the waters of tundra and northern taiga landscapes, whereas in those of mixed-forest landscapes, it recedes to third place giving way to strontium and manganese. In tundra waters, the strontium-to-barium ratio is 2.3; in those of northern taiga, 2.9, and in those of mixed-forest landscapes, 5.5. The copper-to-gallium ratio is, respectively, 4.9, 6.1, and 8.1.

Table 9.11. The Average Concentration of Trace Elements in the Ground Waters of Siberian Boreal and Subboreal Landscapes (after Shvartsev 1978)

Element	Element concentration (μg/l) in ground waters of		
	tundra (360 samples analyzed)	northern taiga (9440 samples analyzed)	mixed forest (500 samples analyzed)
Zn	23.0	31.8	39.5
Sr	21.3	26.3	163.0
Mn	12.3	17.9	55.6
Ba	10.0	9.1	29.4
Li	3.97	6.09	19.0
Cr	2.52	2.16	4.02
Ti	2.34	4.64	21.9
Ni	1.91	1.63	5.29
Pb	1.88	1.16	2.88
Cu	1.70	2.98	5.11
As	0.73	0.99	4.15
Zr	0.68	1.28	2.27
Mo	0.64	0.92	1.28
V	0.50	0.88	1.45
Ga	0.35	0.49	0.63
Sr	0.22	0.50	0.77
Co	0.40	0.24	0.61
U	0.30	0.34	1.01
Ag	0.21	0.37	0.20
Be	0.02	0.04	0.18

The experimental study of migratory metal forms in the waters of forest landscapes has revealed an important role of large organometal complex compounds and colloidal particles (Dobrovolsky and Aleshchukin 1977; Nikitina 1973). Most of the migratory metal forms are represented by particles which, when subjected to dialysis, are incapable of passing across a semipermeable organic membrane. Ionic forms of iron involved in the aqueous migration in northern taiga landscapes are of minor importance as distinct from the metallo-organics accounting for 80% of the total of water-soluble metals in the soil. The breakdown of soluble organic complexes leads commonly to a two-fold increase in trace metal concentration. The dialysis data have shown that more than 50% of the total of trace elements present in waters occur as organic complex compounds and colloidal particles. The percentage of these forms

diminishes with decreasing landscape boreality, whereas landscape waterlogging produces the opposite effect.

The available evidence allows to infer that the aqueous migration of trace elements in forest landscapes is closely related to the geochemistry of organic matter and, specifically, to the formation in the soil of water-soluble organic complex compounds, mainly those of fulvic acids and their derivatives.

During the aqueous migration, the trace elements undergo a systematic redistribution within the successive elementary landscapes in a transect from the watershed to relief depressions. The phenomenon of geochemical conjugation of elementary landscapes has been dealt with in Section 4.3.

The lowland bogs are typical subordinate landscapes in the belt of boreal forests. Migratory forms associated with soluble organic matter are the most characteristic of the forest zone and attain a maximum of their concentration under lowland bog conditions. More than 90% of iron and comparable percentages of manganese, copper, zinc, nickel, chromium, and vanadium occur in the lowland bog waters in the form of soluble organometallic compounds and colloid solutions. The participation of each trace element in the geochemical conjugation is very specific and is dependent on the properties of a migratory form of the trace metal and on the given geochemical landscape conditions.

On the whole, the concentration of most trace elements in the waters of lowland bogs is higher than that in the raised-bog waters. This will be easily seen in comparing the data for bog waters in the central territory of the Zapadno-Sibirskaya Nizmennost'. These data are summarized in Table 9.12.

Table 9.12. The Average Concentration of Trace Elements in Bog Waters of the West Siberia (after Shvartsev 1978)

Element	Element concentration (μg/l) in:	
	raised-bog water (24 samples analyzed)	lowland bog water (41 samples analyzed)
Mn	41.9	52.5
Zn	5.73	9.86
Ba	11.5	9.23
Cu	0.55	1.20
Ti	2.65	1.10
Pb	0.60	0.89
Ni	0.66	0.72
V	0.10	0.19

The heavy metals, owing to their high concentration in bog waters, become actively involved in the biological cycle, which leads to their increased accumulation in the dead organic matter. The metal concentration in the low peatlands of Karelia is higher than that in the raised peatlands: for manganese and zinc, roughly two times; for cobalt, 3-4 times; for molybdenum and copper, 5-6 times. In different regions, the proportion of elements in the peat of lowland and raised bogs exhibits specific features. It has been noted earlier that, as the boreality becomes less pronounced, the pH of natural waters tends to increase and the concentration of dissolved organic compounds, to decrease. Simultaneously, the concentrational contrast of trace elements in low and raised peatlands becomes less distinct.

Another widespread variant of the subordinate elementary landscape in the forest zone is the flood plain. Most of suspended and soluble materials supplied in overland and groundwater run-off to the river valley from the watershed areas are carried away in stream flow beyond the confines of a particular region; however, part of run-off products are retained in the flood plain valley. This process is accompanied by differentiation of trace elements. Heavy metals are retained in the flood plain soils of forest zone rivers, whereas most of more mobile elements (strontium, boron, lithium, fluorine) become involved in the transitional migration to be finally lost into stream flow. As a result, additional metal masses enter the biological cycle in flood plains, and more of the trace elements accumulate in the soil and local vegetation.

10 Biogeochemistry of Extratropical Steppes and Deserts

Extratropical arid ecogeosystems, deficient in atmospheric humidity and characterized by K_h values smaller than 1.0-1.2, occupy a significant part of the World's land. The territory in question includes subboreal zones (steppe, arid steppe, and desert steppe) with total area of $9.23 \cdot 10^6$ km^2, as well as subtropical zones (shrub steppe and desert steppe) with total area of $7.04 \cdot 10^6$ km^2 (Rozanov 1977). These areas do not include subtropical and tropical sandy deserts ($5.77 \cdot 10^6$ km^2) and stony deserts ($8.96 \cdot 10^6$ km^2). Thus, the extratropical arid territory takes about 20% of the World's land. Most of this territory goes to the intracontinental regions of Eurasia and, in part, of North America. The biogeochemistry of arid ecogeosystems exhibits distinctive features which show up in quantitative parameters and dynamics of biomass as well as in the proportion of chemical elements involved in the biogeochemical cycles.

10.1. Biological Cycle of Elements in Arid Vegetable Communities

The vegetation of arid landscapes is chiefly represented by grasses, small shrubs, and shrubs, with their number of xerophytic and ephemeral forms increasing with aridity. At the arid zone periphery, herbaceous phytocenoses are predominant in the natural vegetation cover. In regions with a well-balanced atmospheric humidity (K_h = 1.0-0.75) prior to human activities, of wide occurrence were meadow forb steppes alternating with broad-leaved forests. With the climate becoming more continental, the meadow steppes of Eurasia grade into forb-fescue-stipa and fescue-stipa steppes. In these territories, the native vegetation has in part been destroyed because of human activities, and in part replaced by secondary vegetation. Arid steppes are characterized by the annual rainfall about 350 mm or less: these are absinthum-fescue-stipa steppes and absinthum-fescue steppes. With increasing aridity, small shrubs, mostly those of absinthum species, become relatively numerous. In semidesert and desert regions, halophytic vegetation is also of common occurrence.

The phytomass of arid landscapes is significantly inferior to that of forest landscapes coming down to 1000-2500 tons per square kilometer (by dry organic

matter) in steppes, to 400 tons in deserts, and to 2-3 tons in extra-arid desert landscapes of the Central Asia. The overall vegetation mass of the arid territory of subboreal and boreal belt is by an order of magnitude smaller than that of the forest territory.

The ash content of arid landscape plants is about twice as large as that of plants of humid landscapes. For this reason, although the phytomass of arid landscapes is by one or two orders of magnitude smaller as compared to the forest phytomass, the biological turnovers in both types of landscapes are quite commensurable; the more so, the turnover in steppes is even higher. The structure of biological turnover for the major types of arid ecogeosystems is exemplified by the data in Table 10.1.

A characteristic biogeochemical feature inherent in all the plant communities of steppes and deserts is that their metabolism is more intense as compared to the vegetation types of forest zone. For the steppe vegetation, the time required for a complete renewal of its actual biomass is 2-3 years, whereas in silvan communities, this period extends to 25-50 years. Turnover is the highest in the northern (meadow) steppes, tending to decrease gradually with aridity. The percentage of chemical elements (nitrogen included) annually involved in the biological cycle in northern steppes reaches 55-58% of the total of elements in the biomass; in dry steppes, it is 45-47%, and in half-shrub deserts, less than 35%. The decline in turnover within a system of the biological cycle on passing from humid steppe landscapes to extreme deserts has relevance to the relative contribution of aerial and underground organs to the plant morphology. In the vegetation of meadow steppes, the aerial parts account for 30% of the plant biomass; in dry steppes, it is 15%, and in deserts, 13%. Since the aerial parts are annually renewed almost to 100%, and the roots, to about 30% only, the relative annual gain of biomass in meadow steppes is markedly higher than that in deserts.

The content of ash elements in the biomass of moderately dry steppes is about 60 ton/km^2; in the biomass of arid steppes of Kazakhstan and Altai, it is 25 ton/km^2, and in the biomass of a half-shrub desert of the Ustyurt Plateau, 10 ton/km^2 (Rodin 1965).The annual uptake of ash elements by the vegetation of arid steppes is on the average 10 to 30 ton/km^2, and in a desert, about 4 ton/km^2. The average ash content of the annual growth (production) in arid steppes is 3.5-4.0%, and in half-shrub deserts, about 4%. Based on these data and following the procedure as outlined in Sections 7.2 and 8.1, estimates have been made of the masses of trace elements involved in the biological cycle in dry and arid steppes and deserts. The relevant data are summarized in Table 10.2.

Despite a somewhat arbitrary approach in the calculations, the obtained results provide the possibility to estimate the masses of trace elements involved in the biological cycle in widespread phytocenoses of the World's land arid territory.

Table 10.1. The Mass Distribution for Nitrogen and Total of Ash Elements in the Vegetation of Typical Steppe and Desert Landscapes (after Rodin and Bazilevich 1965)

Landscape type	Content in biomass, ton/km^2		Uptake by vegetation, ton/km^2·year^{-1}		Return to the soil in litter, ton/km^2·year^{-1}	
	nitrogen	ash elements	nitrogen	ash elements	nitrogen	ash elements
Meadow steppes	27.4	90.9	16.1	52.1	16.1	52.1
Dry steppes	10.3	24.2	4.5	11.6	4.5	11.6
Half-shrub deserts	6.1	12.4	1.8	4.1	1.8	4.1

In a particular landscape subject to local geochemical conditions, the concentration of elements in plants and, consequently, the mass of elements involved in the biological cycles may happen to differ appreciably from the calculated values. For example, the concentration of selenium in the vegetation of certain regions of the USA (Colorado Plateau) is so high that the forage grasses are toxic for cattle. In regions of active volcanism, the arid conditions are favorable to the active accumulation of fluorine and a number of other elements. If such is the case, the masses of elements involved in the biological cycle will be significantly larger than those listed in Table 10.2. Strontium, whose ash concentration in the arid landscape vegetation is markedly higher than for the land vegetation *in toto* is also apt to have a more active migration.

The steppe plants feature individual biogeochemical peculiarities. For example, we will refer to Table 10.3 where the data by Skarlygina-Ufimtseva *et al.* (1976) are presented of the concentration of trace elements in typical plants of steppe zone. The sampling site was a hummocky exposed surface covered with thin rubblestone Pleistocene deposits. The annual rainfall was 380 mm, the annual evaporation being twice as large. The samples were collected within an outcrop area of acidic volcanites constituting a uniform bedrock.

Despite the identical growth conditions, the accumulation of trace elements by different plants occurs differently. In feathergrass (*Stipa rubens*), the highest concentrations of manganese and lead have been reported; in the sheep's fescue (*Festuca sulcata*), of titanium and zinc; in the wormwood (*Artemisia marschalliana*), of copper; in the veronica (*Veronica incana*), of nickel. The biogeochemical features of plants under study, typical of a particular locality,

Table 10.2. The Involvement of Trace Elements in the Biological Cycle in Arid Landscapes

Element	Landscape type and annual turnover ($kg/km^2 \cdot year^{-1}$)	
	fescue-stipa and absinthum-fescue-stipa steppes	absinthum-saxaul deserts
Fe	40-120.0	16.0
Mn	41-123.0	16.4
Sr	7-21.0	2.8
Ti	6.5-19.5	2.6
Zn	6.0-18.0	2.4
Ba	5.0-15.0	1.8
Cu	1.6-4.8	0.64
Zr	1.5-4.5	0.60
Ni	0.4-1.2	0.16
Cr	0.35-1.05	0.14
V	0.30-0.90	0.12
Pb	0.25-0.75	0.10
Co	0.10-0.30	0.04
Mo	0.10-0.30	0.04
Sr	0.05-0.15	0.02
Ga	0.01-0.03	0.004
Cd	0.007-0.021	0.003
Total of ash elements	$(10\text{-}30)\cdot10^3$	$0.4\cdot10^3$
Average ash content	3.5-4.0%	4.0%

will accordingly suffer alteration for a locality under different geochemical and landscape conditions. Concentrational variations for uptake of trace elements can be quite significant. Normal, lognormal and complex distributions of the analyzed biogeochemical data have been reported.

In the assessment of an overall effect of geochemical activity of the vegetational cover, of special interest is the composition of groups, rather than of separate genera, of plants forming the main mass of steppe vegetation. Such groups are grasses, legumes, and motley grasses (occasionally referred to as mixed fodder grasses). These groups differ among themselves in concentrational level. In her studies of the composition of these groups in the steppe zone of the Srednerusskaya Vozvyshennost', Savel'eva (1979) has established that

Table 10.3. The Concentration of Trace Elements in the Aerial Parts of Steppe Plants (the South Urals), According to the Data of Skarlygina-Ufimtseva *et al.* (1976)

Element	Element concentration, μg/g (on ash weight basis)				
	Stipa rubens	*Festuca sulcata*	*Poa*	*Artemisia marschalliana*	*Veronica incana*
Mn	1650.0	450.0	225	975.0	650.0
Ti	250.0	934.0	265.0	242.0	900.0
Sr	200.0	131.0	141.0	404.0	250.0
Ba	215.0	210.0	—	47.0	35.0
Zn	750.0	278.0	150.0	273.0	550.0
Pb	110.0	94.0	41.6	33.0	110.0
Cu	35.0	26.0	28.0	175.0	40.0
V	20.0	21.0	15.0	20.0	—
Ni	8.0	14.1	13.3	9.5	16.5
Ag	0.6	0.4	0.4	0.4	—

the grasses are higher in titanium, copper, vanadium, nickel; the motley grasses, in lead and barium; the legumes, in strontium (see Table 10.4).

The concentration of many trace elements in the roots and in the aerial parts of herbaceous vegetation is different. In the root mass of grasses, the concentration of heavy metals is, most commonly, higher than that in the aerial organs. By contrast, in the halo of dispersion of ore deposits, many metals (copper, molybdenum, silver, lead) frequently occur at higher concentration in the aerial organs.

With aridity increasing, various plant species of motley grasses in the vegetational steppe cover become gradually less abundant to finally disappear; in dry steppes, grasses become increasingly replaced by xerophilic half-shrubs and salt-tolerant plants. Simultaneously, the ash content in the plants becomes higher. This is attributed not only to a higher concentration of major ash elements in the plant tissue, but also to the occurrence of finely-dispersed dust adhered to the plants' exterior. In meadow steppes, the ash content of the above ground parts of grasses is smaller than that of the roots; in dry steppes, the masses of the two are nearly equal; in desert, the ash content in the roots is predominant. In particular, the ash content of both the underground and above ground parts of the wormwood thriving in the steppes of Yuzhnyi Ural (the South Urals) and North Kazakhstan is 7-10%, whereas for the same species

Table 10.4. The Concentration of Trace Elements in Major Plant Species of the Steppe Zone (Srednerusskaya Vozvyshennost')

Element	Element concentration, μg/g (on ash weight basis)		
	legumes (clover)	grasses	motley grasses
Ti	203.6	627.8	490.6
Mn	550.0	1092.3	1093.3
Sr	1616.7	458.8	971.4
Ba	341.7	255.0	729.9
Ni	20.5	35.0	26.1
Pb	14.9	19.2	20.9
Zr	10.0	13.6	20.0
V	9.1	50.6	31.4

in the Transcaspian deserts, the ash content of the aerials is 12-16%, and of the roots, 8-9%. In the salt-tolerant plants, this contrast is still more striking. To be noted, the high ash content is not necessarily concomitant with the higher concentrational level of trace elements.

In deserts, similar to steppes, the plants exhibit distinctly their biogeochemical specificity. We have studied the distribution of trace elements in the vegetational cover of the desert Ustyurt Plateau (Dobrovolskii 1961). Here the major plant species are wormwood (*Artemisia terrae albae*) and saxaul (*Anabasis salsa*). In rubblestone territories, of common occurrence is the dense shrubbery of *Salsola anbuscula*. Most elements found in the wormwood occur in their highest concentration; however, in the saxaul, the number of detected ash elements (mostly, those constitutive of water-soluble salts) is about twice as large. In the salt-tolerant Russian thistle, strontium is the only one to occur in elevated concentration. In the roots of wormwood and saxaul, higher concentrations of manganese, copper, molybdenum, and strontium have been established, that is, of elements actively involved in the biological migration. The aerial parts contain more titanium, vanadium, and zirconium which are, however, modest contributors to the biological migration of elements. Possibly, their presence should be in part attributed to the surficial finely-divided silicate dust, as has been noted above.

Despite the quantitative variability of salts and silicate dust particles in the plants of arid landscapes, one will easily discern a trend towards the selective

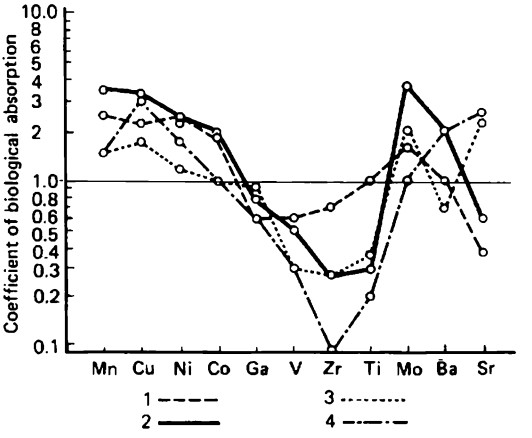


Fig. 21. Biological uptake of trace elements by plants of the Ustyurt desert
1—wormwood (*Artemisia terrae albae*), aerial parts; *2*—roots; *3*—anabasis; (*Anabasis salsa*), aerial parts; *4*—roots

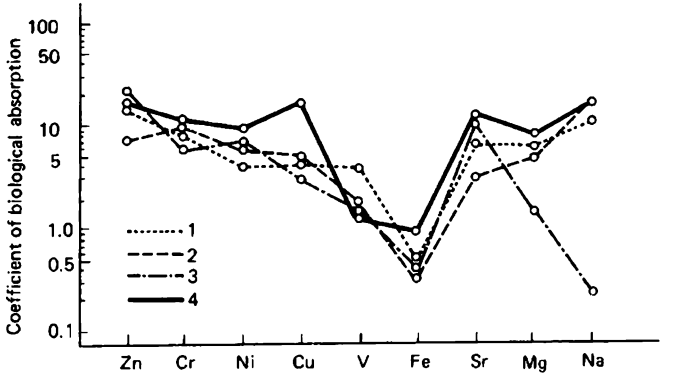


Fig. 22. Biological uptake of chemical elements by cenospecific plants of extra-arid Gobi desert
1—Haloxylon ammodendron; 2—Iljina regeli; 3—Ephedra Przewalskii; 4—Anabasis brevifolia

absorption of trace elements. Calculations of the coefficient of biological absorption (K_b) have shown that the elements contained in the vegetation of steppes and deserts are in an equal measure susceptible to the action of general biogeochemical factors. The most actively involved in the biological cycle are strontium, copper, molybdenum, and zinc. Their values of K_b are never less than 1. Titanium, zirconium, and vanadium are poorly taken up, with their values of K_b often dropping below 0.1

Shown in Figs. 21 and 22 are graphs characterizing the rate of absorption of elements by the vegetation of steppes and deserts.

The general trend towards concentrational increase of ash elements in the plants on grading of the steppe landscape to the desert does not seem to affect the K_b values appreciably.

10.2. Biological Cycle in Extra-arid Deserts

The biogeochemical processes that occur under the least favorable conditions for life of extra-arid deserts are of considerable interest both from a theoretical point of view and in the aspect of their potential practical applications. Such extreme deserts extend over a vast territory in the middle of the Eurasian supercontinent. The Gobi is one of the most severe deserts of Central Asia. The rainfall in the western part of the Gobi desert is commonly 20 to 50 mm per year, in sharp contrast to the evaporation of 1250 mm/ year. The surface of gentle piedmont slopes and intermontane valleys has the aspect of a compact rocky crust, the so-called desert armor. This armor, composed of the pebbles of metamorphic and volcanic rocks with the lustrous black glaze of "desert varnish," defies even the timid suggestion of an eventual existence of life in this forlorn expanse. Periodically, at an interval of about 10 years, the atmosphere over the Gobi desert becomes invaded with moist air masses which discharge in profuse rains. The run-off streams erode numerous shallow depressions (the so-called sairs) dissecting the surface of the rocky hammada into separate extended stretches. A larger part of the Gobi desert is covered with a sparse vegetation represented by shrubs and undershrubs.

Among the former, predominant are the haloxylon (*Haloxylon ammodendron*), ephedra (*Ephedra Przewalskii*), (*Zygophyllum xanthoxylon*), (*Reamuria soongoriea*); among the undershrubs, one should mention *Anabasis brevifolia* and *Sympegma regelii*. At the periphery of the desert zone, grasses (*Stipa glareosa*) and onions (*Allium mangolicum* and others) are encountered. In the southernmost regions, the extra-arid landscapes of rocky hammada are either entirely devoid of vegetation, or provide a scant residence to rare specimens

of *Iljinia regelii*, 1.3 specimen per 100 m^2 (Kazantseva 1986). In the sairs, separate specimens of haloxylon and ephedra are encountered.

On the basis of our explorations in the field followed by analytical laboratory analysis, we have outlined major features of the mass exchange of chemical elements in the biological cycle of extra-arid deserts.

As has been established, plant specimens from extra-arid landscapes contain alkali, alkali-earth elements, and iron at concentrations of tenth and hundredth fractions of one percent; manganese, zinc, strontium, and, partly, chromium, $10n$ μg/g; copper, nickel, and vanadium, n μg/g; lead and cobalt, as a rule, less than 1 μg/g (on a dry weight basis for plants rinsed in doubly distilled water prior to analysis).

With these values in mind, it is important to remember that the distribution of elements over the plant parts is different. Sodium occurs in the green organs at a significantly higher concentration than in the stems of shrubs and undershrubs, whereas the exact opposite holds for calcium. Strontium is distributed in a manner much similar to that of calcium, with its concentration higher in the stem and twigs. Also, iron and manganese occur in higher concentrations in the stem and twigs. The distribution for other heavy metals follows a less straightforward pattern. For example, higher concentrations of zinc were detected in the twigs of *Iljinia regelii* and in the stem of haloxylon; in ephedra, the concentration of this metal was highest in the leaves. The highest concentrations of copper were found in the shrub leaves (ephedra and haloxylon); in *Iljinia r.*, the stem was higher in copper.

The involvement of chemical elements in the biological cycle from the soil, expressed in terms of coefficient of biological absorption is shown in Fig. 23. The highest values of K_b as estimated by the annual growth of green biomass of the desert plants of Zaaltaiskaya Gobi have been found for zinc (20-40) and sodium (up to 15); for strontium, chromium, copper, nickel, and vanadium, K_b = 1 to 10; for iron and manganese, K_b is less than 1.

A comparison of the K_b values for the World's land vegetation (see Table 1.6) and those of the desert plants will reveal that *Haloxylon ammodendron* and *Iljinia regelli*, the major representatives of the cenosis in the extra-arid deserts of Zaaltaiskaya Gobi, are very active in taking up sodium and, to a somewhat lesser extent, of magnesium and strontium. This is an immediate consequence of the extremely low rainfall level, enhanced transpiratory activity of plants, and high salt concentration in the soils of extra-arid landscapes. Noteworthy, the K_b's of certain heavy metals are higher than their average K_b values for the production of land vegetation. Presumably, this is associated with the presence of easily mobilized forms of metals in the soils of extra-arid landscapes, primarily, those metals whose percentage in the soil-forming substrate of Gobi deserts is higher than their crustal abundance in the granitic layer of lithosphere (zinc, copper, chromium, and vanadium).

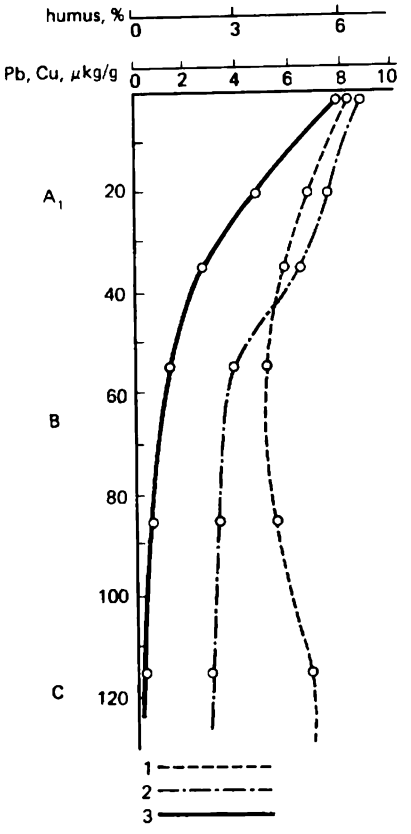


Fig. 23. Distribution of mobile forms of zinc (curve *1*), copper (curve *2*), and humus (curve *3*) down the chernozem soil profile

The paleogeographic evolution of South Mongolia during the Cenozoic was remarkable for a progressive desiccation. This process in the Gobi as well as in other deserts of the Central Asia was, on the one hand, inhibitory for the speciation (Vavilov 1931), but, on the other hand, it was favorable to the preservation of species and forms well adapted to the geochemical conditions of an arid landscape. For this reason, along with geobiochemical features common to the vegetation of the Gobi deserts, certain plant species reveal specific geochemical peculiarities. For example, with all the plants studied, the highest concentration of iron was detected in the undershrub stems, while the green organs contained the highest amount of sodium. The highest concentration

of strontium was typical of *Anabasis brevifolia*. Perhaps, this may be regarded as a systematic character, taking into consideration that the effect of selective strontium uptake was earlier observed by us for *Anabasis salsa* in the Ustyurt desert (Dobrovolskii 1961).

The shrubs exhibit compositional specificities. Some of them, as representatives of the ancient arid flora, have developed mechanisms aimed at counterbalancing the high content of salts in the environment. For example, in *Ephedra Przewalskii* thriving in the sairs of lifeless rocky deserts an unexpectedly low content of the major salt-forming element, sodium, was found, simultaneously with the presence of strontium in very high concentration. *Zygophyllum xanthoxylon* and *Coriopteris mongolica* were reported to contain zinc in concentrations maximal for the desert plants. This fact and others attesting to a geochemical specialization of the flora of the Zaaltaiskaya Gobi, evolved under specific environmental conditions, stand in need of a thorough and more detailed investigation.

The exudation of water-soluble salts by plants in respiration is a very important geochemical factor under the conditions of extra-arid deserts. The salt exudates are either blown away by the wind contributing thereby significantly to the aerosol composition, or washed off in rainfall to constitute a specific flux of chemical elements in the biological cycles.

The following concentrations of water-soluble forms of elements have been detected in the green organs of plants thriving in the extra-arid deserts of the Zaaltaiskaya Gobi (in μg/g of dry vegetable matter): sodium and potassium, tens of thousands in *Haloxylon ammodendron* and thousands in *Iljinia regelli*; calcium and magnesium, less by one or two orders of magnitude; iron, several units in *Iljinia r.* to more than 100 in *Ephedra Przewalskii*; manganese, 3 to 19; strontium and zinc, 1-2; copper and nickel, tenth fractions of a unit. Cobalt, chromium, and, occasionally, lead were present in trace amounts; no vanadium was detected in the samples examined.

The water-soluble compounds of sodium and potassium occur in roughly the same amounts as the insoluble species of these metals tightly held in the plant tissues. The rinsings from the green current twigs of haloxylon were found to be higher in sodium than the vegetable matter; as to magnesium, only a smaller portion of it was detected in the rinsings. As distinct from the haloxylon, the green shoots of *Ephedra Przewalskii* exude very little water-soluble sodium compounds, whereas the amount of magnesium salts in the exudates was appreciably higher. These findings provide evidence for different mechanisms acting in response to the excess amount of various chemical elements in the shrubs in question which are the most well-adapted plants thriving under severe conditions of the extra-arid deserts of the Zaaltaiskaya Gobi.

The water-soluble forms of heavy metals and strontium which are lost into the wash-off account on the average for 5-10% of the total of these elements.

No direct proportionality between the contents of water-soluble and tightly held forms of elements has been found, but despite the fact, there is reason to suspect a relationship between them. For instance, the elevated concentration of strontium in the green organs of *Ephedra Przewalskii* and of iron and manganese in *Haloxylon ammodendron* bears relevance to the amount of soluble forms of these metals.

The results of analysis have shown that the composition of water-soluble compounds varies systematically with decreasing aridity. For one thing, this is reflected in the decreased content of sodium in the water rinsings from the plants sampled in a transect from the extra-arid landscapes towards the desert periphery. It is noteworthy that the rinsings from the aerial parts of the plants typical of steppes (feathergrass and wormwood) contain sodium in concentrations a hundred times smaller than those in the rinsings from the green organs of the plants thriving in extra-arid deserts (*Haloxylon ammodendron, Iljinia regelii, Anabasis brevifolia*). Supposedly, the intense exudation of water-soluble compounds by the green organs of plants is a process which counteracts the detrimental effect arising from the high concentration of both salts and trace metals in the soil solutions of extra-arid deserts.

The available evidence allows us as a first approximation, to estimate the masses of chemical elements involved in the biological cycle operative in the extra-arid ecogeosystems of the Gobi Desert. According to the data of Kazantseva (1986), the annual production of overground biomass of the iljinia community in the hammada is 220 kg/km^2 of dry matter; that of the haloxylon-iljinia community confined to the sairs, 247 kg/km^2. The production of the phytocenosis of xerophytic shrubs *Haloxylon ammodendron* and *Ephedra Przewalskii* confined to relatively large sairs is about 800 kg/km^2. The data on the mass transport of elements are summarized in Table 10.5; for comparison, presented therein are also analogous data for a plant community typical of a less arid landscape in the periphery of a desert and represented by the species *Anabasis brevifolia* and *Stipa glareosa.*

The obtained estimates, despite their obviously approximate nature, give an idea of the involvement of chemical elements in the biological cycle in the extra-arid deserts of the Zaaltaisakaya Gobi (Transaltai Gobi). In autonomous ecogeosystems, the mass of sodium involved in the biological cycle does not exceed 4000, and that of magnesium, 1000 grams per square kilometer per year. For iron, it is close to 100, and for most heavy metals, it is about 1-4 grams per sq. kilometer per year. In the geochemically subordinate sairs landscapes which receive additional moisture and chemical elements in rainfall, the turnover rate becomes larger. In such a particular case, the involved masses of metal may reach kilograms per sq. kilometer for sodium and magnesium, and tens of grams per sq. km for other metals. In the peripheral zone of deserts, the overall increase in the turnover of masses involved in the biological cycle

Table 10.5. The Involvement of Trace Elements in the Biological Cycle in Extra-Arid Landscapes of the Zaaltaiskaya Gobi (Transaltai Gobi)

Landscape and plant community	Turnover of trace elements, g/km² per year									
	Na	Mg	Sr	Fe	Mn	Zn	Cu	Ni	V	Cr
Extra-arid deserts: *Iljinia regelii* community in the desert plain	3960 / 1580	770 / 20	8 / 0.1	110 / 1	7 / 0.3	4 / 0.2	1 / 0.1	2 / 0.1	2 / 0.1	3 / 0.1
Haloxylon ammodendron-Iljinia regelii community in the sair	28150 / 3040	8650 / 620	107 / 3	2200 / 119	205 / 54	91 / 7	16 / 0.3	14 / 0.2	0.35 / 0.1	36 / 0.1
Haloxylon ammodendron-Ephedra Przewalskii community in the sair	91200 / 101600	36000 / 2000	347 / 9	7130 / 387	665 / 152	294 / 22	50 / 0.8	0.44 / 0.7	114 / 0.1	116 / 0.1
Desert steppes: *Anabasis brevifolia* community with *Graminaeae* in the desert plain	271800 / 11325	60300 / 760	1739 / 11	26440 / 32	1228 / 77	658 / 16	298 / 0.1	170 / 0.1	97 / 0.1	254 / 0.1

Note: Numerals in the numerator refer to trace elements tightly held in plant tissue; those in the denominator, to trace elements constitutive of water-soluble forms.

is attended by a change in the proportion of the elements taken up because of a different geochemical specialization of the plant cenotypes. Therefore, the turnover for some elements (magnesium, vanadium, chromium) rises but slightly in comparison to their turnover in extra-arid deserts, whereas the turnover for other elements (strontium, zinc, copper) increases several times.

It is to be inferred from the available evidence that the amounts of heavy metals as released by the green organs of plants in a water-soluble form are rather small, reaching tenth fractions of a gram per sq. kilometer per year in the autonomous landscapes of extreme deserts. In the sairs, under the conditions of a subordinate regime, the turnover of water-soluble compounds reaches 100-300 g/km^2 per year for iron and manganese, more than 20 g/km^2 for zinc, grams per sq. kilometer for strontium, and tenth fractions of a gram per sq. kilometer for other metals. The excess amount of sodium which is released by the phytocenoses of autonomous landscapes in extra-arid deserts does not exceed 1-2 kg per sq. kilometer per year. In the sair landscapes, the release of metals proceeds at a greater rate, reaching 100 kg/km^2 per year or more; for sodium, the release was occasionally observed to be even higher than the content of this metal in the annual growth of phytomass. The most active involvement of sodium in the biological cycle is known to be in the plant communities of *Anabasis brevifolia*, at the periphery of the Zaaltaiskaya Gobi.

10.3. Specificity of Soil Biogeochemistry in Arid Landscapes

The soils of arid landscapes with relatively high atmospheric humidity, typical of meadow and moderately dry forb steppes, is characterized by a high biotic activity. An enormous number of invertebrates promptly disintegrate and digest the plant remains and mix them with the mineral matter of soil. The dispersal of organic detritus is made easier owing to that the larger part of the die-off products of herbaceous vegetation are retained in the soil rather than become accumulated on the soil surface as this commonly occurs in the forests.

In the soils of arid landscapes, the soil-biological population of microorganisms undergoes a significant change. Fungi, which play a decisive role in the conversion of plant remains in the forest landscapes, make way for bacteria. The microbiological and biochemical transformation of organic matter in the steppe soils leads to the predominant occurrence of sparingly soluble and therefore little mobile humic acids. The humic acids form complexes with metal cations preventing thereby their removal from the soil. The metal migration is further hampered by the impeded water regime of the steppe soils and by their saturation with calcium ions. The latter circumstance provides for a tight

coagulation of clots and films of humic acids as well as of finely-dispersed mineral particles which coalesce to form compact organomineral aggregates, the so-called peds. Owing to numerous and diverse biological and physico-chemical factors, the biolatent system of steppe soils is favorable to the binding and accumulation of heavy metals and other elements of variable valence in the uppermost humus horizon. The concentration of chemical elements in the soil tends to decrease slightly down the profile, in parallel with the decrease in bacterial population and humus content. This is illustrated in Fig. 24.

A larger part of trace elements in the steppe soils are bound with highly-dispersed mineral particles, and a lesser part, with organic matter; the exchange and water-soluble forms account for less than 1% of the total content of an element in the soil. Specific forms of trace elements that occur only in the soils of arid landscapes are associated with carbonate, gypsum, and chloride-sulfate water-soluble recent formations.

As an example, the data in Table 10.6 for cobalt are illustrative of the variation of the overall concentration of a metal and its major forms down the profile of chernozem and dark chestnut soils. To be noted, the soils in question are found in nature reservation territories of the steppe zone of the European part of Russia and have never been used for agricultural purposes. The deep chernozem was sampled for analysis in the territory of the Central chernozem reservation "Streletskaya Steppe," and the dark chestnut soil, in the territory of the Askania-Nova reservation.

The water deficit in arid zones is an inhibitory factor for biogeochemical processes. According to the data of Chernov (1975), the wet biomass of soil invertebrates in the meadow steppe and forest steppe is 70 tons per sq. kilometer, in the semidesert, it is 0.6, and in the rocky desert, 0.2-0.4 tons

Table 10.6. Distribution of Cobalt and Its Major Forms Down the Steppe Soil Profile (according to the data by Zyrina and Titova, 1979)

Soil horizon	Total concentration, mg/kg		Fraction (%) of the total cobalt content retained in:					
			humus		clay matter		carbonates	
A	9.2	(11.3)	30.4	(25.7)	43.5	(49.5)	—	—
B	9.4	(10.4)	22.2	(14.4)	48.0	(43.3)	—	(11.5)
C	8.5	(9.4)	4.7	(5.3)	61.2	(60.7)	10.9	(6.4)

Note: Free numerals refer to the typical deep clay-loamy chernozem overlying the loess; the parenthetical numerals refer to the dark clay-loamy soil overlying the loess.

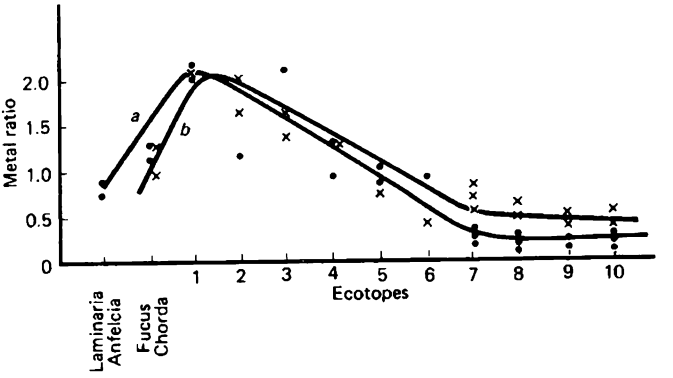


Fig. 24. The Na/K (curve *a*) and Mg/K (curve *b*) ratios in inland plants as a function of distance from the coast line (the White sea, Bolshoy Solovetsky Ostrov)

1— halophytes o tidal zone; *2*—halophytes of boundary tidal zone strip; *3*—plants of shallow marshes; *4*—vegetation thriving on decayed algal ridges; *5*—pioneering vegetation of beach zone; *6*—draining vegetation of peripheral beach zone; *7*—tundral seacliff zone vegetation; *8*—bush vegetation; *9*—birch dwarf forest; *10*— birch-spruce taiga forest

per sq. kilometer. The humus content in the soil of dry steppes goes down as low as 2-4%; in the gray brown soil of desert, it is seldom higher than 1%.

The overall concentration of trace elements in the soil of steppes and deserts is determined by the content of these elements in the soil-forming rocks. Also, the water-soluble forms become an increasingly important factor in desert soils. One will become aware of an analogy between the increased content of elements in dead organic matter in the soil as a function of enhanced boreality of forest landscapes and the increased content of soluble forms of elements in the soil of dry steppes and deserts as a function of enhanced aridity. A comparative study of the soil profile of the deserts in the Central Asia has shown a higher content of water-soluble forms for all elements in the upper horizon. Strontium is the only element whose concentration tends to increase down the soil profile.

The main factors for the accumulation of water-soluble forms of elements in the upper soil horizon of deserts are evaporative concentration and the transpiration of plants. Along with this, the higher alkalinity of dry landscape soils is favorable to the mobilization of finely-dispersed mineral and organic suspensions. This fact provides a plausible explanation of the occurrence of zirconium, titanium, gallium, yttrium and their congeneric elements in the aqueous extracts of desert soil samples.

The distribution of chemical elements along the soil profile of extra-arid landscapes of the Gobi Desert is similar to that for the deserts of the Central

Asia and Ustyurt Plateau. The overall elemental content along the soil profile of the Gobi Desert is very little varied. For most metals, a single extraction with 10% HCl yields 5-10% of their total content; iron and manganese, as distinct from the rest of elements, are extracted in higher concentrations. The extraction yield for strontium reaching as high as 20-25% should presumably be attributed to the partial dissolution of the recent gypsum and carbonate formations. The concentration of most metals in 10% HCl extracts is maximal for the top soil horizon (unconsolidated layer). As distinct, the concentration of strontium is higher in the lower part of soil profile, in the gypsum horizon, which is typical of the soil of the Central Asia deserts.

10.4. Biogeochemical Processes in Relation to Aqueous and Atmospheric Migration of Elements

Part of chemical elements become mobilized by soil processes to be finally supplied to the surface and underground waters. As is known, the mineralization of natural waters grows with increasing aridity. The concentration of some trace elements correlates with the overall mineralization; no such relationship has been found for other elements. Comparison of the trace element contents in surface waters in the territory of the Ukrainian crystalline shield has shown that the concentration of some elements varies systematically on passing from forest to steppe landscapes. The relevant data are summarized in Table 10.7. For zinc, the average concentration in the water of forest landscapes is 11 μg/liter, of forest steppe landscapes, 28, and of steppe landscapes, 36. For strontium, the respective concentrations are 36, 68, and 128 μg/liter. Simultaneously, the concentrational variation for some elements, for example, zirconium, defies any regularity, whereas for manganese, its concentration is higher in the forest water than in the steppe water.

A point to be noted is that the coefficient of aqueous migration (K_w) for certain chemical elements in the surface and underground waters of arid regions is smaller than that for the forest water. Two reasons for the fact seem to be plausible. First, owing to the biotic activity of edaphic microorganisms, a large number of soluble humic acids are synthesized in forest soils; these acids form complexes with trace elements providing thereby the major possibility for aqueous migration of trace elements. Second, in the arid landscapes, because of the deficient atmospheric humidity, a large part of water-soluble forms of elements in the upper soil horizon fail to enter the aqueous migration.

The lack of tree vegetation and the lean protective layer of grass and half-shrub vegetation are the major reasons that a large mass of soil particles become entrained into the atmospheric migration.

Table 10.7. Trace Elements in the Surface Waters of Forest, Forest-Steppe, and Steppe Landscapes of the Ukrainian Crystalline Shield (based on the data of Mitskevich, 1971)

Element	Element concentration (μg/liter)		
	forest landscape	forest-steppe landscape	steppe landscape
Sr	36.0 (0.5)	68.0 (0.9)	128 (1.6)
Ti	40.0 (13.3)	94.0 (31.3)	106.0 (35.3)
V	2.7 (3.0)	6.0 (6.7)	4.0 (4.4)
Cr	5.4 (5.4)	8.0 (8.0)	9.0 (9.0)
Cu	2.4 (0.3)	12.0 (1.7)	10.0 (1.4)
Pb	4.8 (4.8)	3.0 (3.0)	3.0 (3.0)
Zn	11.0 (0.6)	28.0 (1.4)	36.0 (1.8)
Sn	3.5 (7.0)	4.0 (8.0)	1.5 (3.0)
Zr	4.2 (1.6)	9.0 (3.5)	2.0 (0.8)
Mn	158.0 (16.0)	94.0 (9.4)	126.0 (13.0)

Note: The parenthetical value is the ratio of the given concentration of an element to the average concentration of the element in the world rivers.

Since the water-soluble forms of elements are in significant amounts confined to the surface soil horizon of dry steppes and deserts, they are actively supplied to the atmosphere.

The low rate of aqueous migration of some elements in the arid zone and their resultant accumulation as components of water-soluble salts and disperse particles at the soil surface are very essential factors for the geochemistry of aerosols. On the continent, the aerosol geochemistry is to a significant extent determined by the development of vegetation and by the biogeochemical processes that occur in the soil. The average mineralization of the rainfall in the forest zone of Russia is 17-20 μg/liter, in the steppe territory, 45-50 g/liter, and in the deserts, over 150 g/liter.

Despite the smaller rainfall over the arid territory in comparison to the forest belt, the arid landscapes receive more salts from the atmosphere than the areas of excess humidity. It may be accepted, on the basis of the analytical data of Zverev *et al.* (1973) for 1500 soil samples collected at 115 sites, that the atmospheric supply of salts in the boreal forests is 7 to 10 ton/km^2, in the steppes, about 18, and in the deserts, 22 ton/km^2 per year.

The mineralization of atmospheric precipitation is in a complicated manner associated with the content of trace elements. The concentration of many elements in rainfall is subject to wide and little consistent variations; however, for a number of elements such as potassium, sodium, and strontium, the concentration is seen to rise systematically with overall mineralization.

By virtue of the fact that the elemental content of water-soluble forms accounts on the average for about 50%, it becomes apparent that the total mass of trace elements in the lowermost tropospheric layer over the arid areas is much larger than over the forest zone.

A larger part of continental aerosols are carried away by the wind from the soil surface and aerial organs of plants to become involved in the cycle of multiply repeated precipitation and reentrance into the atmosphere of arid regions. In this context, it appears expedient to assess the global migration of dust masses whose major sources are dry steppes and deserts.

Regrettably, no systematic studies of the transport and precipitation of airborne dust over the World's land has yet been carried out. There has been reported evidence for separate, mostly arid, regions. More complete data are available for the ocean. The average of precipitated mineral dust over the pelagic part of the World's ocean is about 3 tons per sq. kilometer. The pelagic zone takes about 90% of the oceanic water surface ($324 \cdot 10^6$ km^2), and the circumcontinental shelf, about 10% ($36 \cdot 10^6$ km^2). The area of continental glaciers (mainly, those of the Antarctics) is $15 \cdot 10^6$ km^2. Consequently, $1.1 \cdot 10^9$ tons of continental dust falls on the surface of the pelagic zone and glaciated areas, and $0.54 \cdot 10^9$ tons, on the oceanic surface of continental shelf, making a total of about $1.7 \cdot 10^9$ tons per year.

About one-third of the total mass of dust particles supplied to the troposphere is carried away beyond the World's land. The major sources of dust (blow-off regions) are arid areas whose surface is destitute of vegetational cover that might have prevented a massive carry-over of fine particles by the wind. The mass of dust annually entrained into the troposphere from the World's land surface is close to $5.5 \cdot 10^9$ tons. This mass, related to the area of arid territories (about $60 \cdot 10^6$ km^2), gives an average value for the entrainment of dust from a unit area of arid landscape of about 90 ton/km^2 per year. In reality, the actual value is somewhat higher because a certain amount of dust is additionally carried away from the surface of territories within the humid climatic zone. One may presume, with reference to the available data, that the average entrainment of dust from a unit area of arid territory must be at least 70 ton/km^2 per year.

The average precipitation of dust onto the surface of humid landscapes intact by human activities is 18-20 ton/km^2 per year, and the total precipitated mass is $1.3\text{-}1.5 \cdot 10^9$ tons annually. As has been noted above, about $1.7 \cdot 10^9$ tons of dust per year is carried over from the World's land to the ocean. Consequently,

at least $2.5 \cdot 10^9$ tons per year (which is equivalent to about 40 ton/km^2·year^{-1}) is returned to the arid areas. The transportation of such huge masses of disperse mineral matter cannot leave the biological processes unaffected. The permanent occurrence of substantial amounts of finely-divided mineral particles incorporated into the outer tissues of plants of dry steppes and deserts is an important, but little studied factor in the biogeochemical cycles of trace element mass exchange.

11 Biogeochemistry of Tropical Land

The tropical ecogeosystems are the most rich in energy. The belt situated between 30° N and 30° S receives about 60% of the solar radiation incident on the Earth. Owing to this, the cyclic mass exchange of chemical elements in this belt proceeds at a quite high rate. The cyclic processes extend to a vast territory, more than half of the World's land nonmountain territories. The total area of tropical landscapes amounts to some $40 \cdot 10^6$ km^2, excepting the rocky and sandy deserts with strongly suppressed life.

The history of the tropical land development exhibits specific features that have left an impression on the current biogeochemical processes.

11.1. Biological Cycle of Chemical Elements in the Tropics

The bioclimatic conditions of tropical territory are quite diverse. The tropics, deeply rooted in the layman's mind as a continuous belt of dense jungle, are in reality very far from this romantically mistaken belief.

The varying proportion of atmospheric precipitation and evapotranspiration, duration of dry and rainy seasons create a wide spectrum of landscapes — from extra-arid deserts to permanently humid rain forests. Drought-deciduous (during a prolonged dry season) high-grass broken forests are common to landscapes where the annual evaporation is in excess of the annual rainfall. Typical of more arid conditions are clusters of thinly growing trees alternating with open spaces of herbaceous vegetation. With increasing aridity, trees are replaced by thornbush, and the rank, tall herbaceous cover grades down to low-growing grass vegetation with shallow soil coverage.

The proportion of areas of different atmospheric humidity varies from continent to continent. Arid territories are predominant in Australia, in a large part of India, and less in Latin America. In an equatorial belt of Africa between 6° N and 6° S, the territories of varying atmospheric humidity are distributed in the following manner:

Annual rainfall, mm	
1800	22
1000-1800	48
600-100	12
200-600	16
200	2

It is to be inferred from these data that the rainfall forests occupy about 1/5 of the African equatorial belt, whereas its larger part is dominated by light forests and tall-grass savannas. In the rest of the African continent, are typical more or less arid landscapes, including those nearly desertic, with the rainfall less than 200 mm per year.

According to the data by Rozanov (1977), the tropical forests of all types occupy 20448 thousand square kilometers, or 13.33% of the World's land; the savanna zone, 14259 thousand square kilometers (9.56%); tropical deserts, and 4506 thousand square kilometers (3.02%). In those estimates, the areas taken by sandy deserts, rocky lifeless deserts, and solonchaks were ignored.

The tropical rain forests constitute the most powerful plant formation. The abundance of heat and moisture provides for the largest biomass among the World's land biocenoses, averaging 50 000 ton/km^2 of dry matter, occasionally reaching 170 000 ton/km^2. A factor that sets a limit on the biomass growth is solar energy required for photosynthesis. To maximize the use of light energy, there are found, beneath the top cover of tall (30-40 m) trees, several lower storeys of trees well-adapted to stray light. A large part of died-off and fallen leaves from tall trees are entrapped for assimilation by numerous epiphytes. For this reason, the chemical elements contained in the leaves reenter the biological cycle in bypassing the soil. In tropical rain forests, the vegetation continues the whole year round, the annual production being on the average 2500 ton/km^2.

The annual supply of CO_2 to the atmosphere from the ecosystems of tropical forests is quite significant falling, according to Detwiler and Hall (1988), into a range of 0.4 to $16\,10^9$ ton/year of carbon.

The biogeochemical specificity of tropical rain forests is that almost the total of chemical elements needed for sustenance of the huge vegetable mass are contained in the plants themselves. The biogeochemical metabolic cycle is essentially closed. An uncontrolled intervention into a tropical rain forest (felling or slashing for commercial purposes) leads, along with the destruction of trees, to a breakdown of the entire system of the biological cycle with its thousands of years of the evolutionary history: the deforestation will leave behind a barren soil.

The biogeochemical situation in light deciduous tropical forests and savannas is similar to that in the deciduous forests of temperate climate; however, a major distinction is that the periodical inhibition of biogeochemical activity in the temperate climate is associated with the temperature lowering, and in the tropical climate, with the lack of rains and seasonal moisture deficit. The biomass of dry savannas is typically 200-600 tons per sq. kilometer, the mass of annual sheddings being 1/3 to 1/4 of that amount. The annually shed vegetation less than 150-200 tons per sq. kilometer is typical of tropical desert conditions. The biomass of deciduous tropical forests of varying humidity and

that of tall-grass parkland savannas are intermediate between the biomasses of rain forests and dry savannas.

According to the available evidence (Rodin *et al.* 1965), the distribution and dynamics of vegetable mass of a tropical rain forest are characterized as follows (all values in ton/km^2):

Biomass:	
total	52000
nitrogen	294
ash elements	814
Annual production:	
total	3250
nitrogen uptake	43
ash element uptake	160
Litter production:	
total	2500
nitrogen	26
ash elements	128
average ash content	4.6%

Noteworthy, the concentration of chemical elements in the trunk wood and twig wood of tropical trees is, as a rule, lower than that in the leaves in accounting for the bulk of shed materials. The nitrogen concentration in wood is seldom as high as 0.5% (by dry weight), whereas in the leaves it is usually about 2%. The concentration of calcium, potassium, magnesium, sodium, silicon, and phosphorus in the leaves is commonly several times that in wood (see Table 11.1). The concentrations of elements in the tree leaves and in the herbaceous vegetation (abundant in light deciduous forests) do not differ significantly. The concentration of most trace elements in tree leaves and grasses is higher than their concentration in wood, excepting barium and, especially, strontium whose wood concentrations are higher.

Based on the available data, we have taken the average sum total of ash elements in the rain forest biomass to be equal to 800 tons per sq. kilometer; the turnover of these elements in the biological cycle has been taken as 150 ton/km^2 per year. For light forests, the respective average values are 200 tons per sq. kilometer and 50 ton/km^2 per year. Starting from these estimates, we have calculated approximate masses of trace elements annually involved in the biological cycle; the relevant data are presented in Table 11.2.

The concentrational levels of trace elements in the soil-forming substrate of different regions of the tropical land are not the same. Consequently, the element concentrations in plants are also different. For example, in grasses of the family *Gramineae* collected in an outcrop area of crystalline rocks of the Precambrian basement in East Africa, the copper concentration is $71 \cdot 10^{-4}$%, whereas in analogous grasses thriving on a volcanic laval soil it is $120 \cdot 10^{-4}$%.

Table 11.1. Concentration of Ash Elements in the Equatorial Vegetation of East Africa (Dobrovolsky 1975)

Sample number	Elements, % (on a dry weight basis)										"Pure ash"	Mineral dust admixture
	Si	Al	Fe	Mn	Ti	Ca	Mg	Na	P	S		
52	2.27	0.41	0.40	0.008	0.006	0.24	0.12	0.03	0.06	0.01	7.29	3.21
76	0.05	0.01	0.02	0.001	0.001	0.29	0.02	0.01	0.02	0.04	0.79	0.40
42	1.06	1.87	1.48	0.05	0.07	0.45	0.27	0.22	0.06	0.04	9.87	11.33
210	0.69	0.01	0.08	0.02	0.001	0.08	0.08	0.05	0.08	0.06	6.32	0.68

Samples: No. 52, broken herbaceous cover of low-grass savanna with the predominance of the genera *Sporobolus, Cynodon, Kyllinga*, in north-western Tanzania.
No. 76, the trunk of *Podocarpus*, rain forest on the south-facing slope of Kilimanjaro, Tanzania.
No. 42, forest litter of the rain forest on the south-facing slope of Kilimanjaro, Tanzania.
No. 210, the stems of papyrus (*Cyperus papyrus*), the White Nile floodplain near the riverhead, Alberta Lake, Uganda.

Table 11.2. Involvement of Trace Elements in the Biological Cycle of Tropical Forests

Element	Element turnover, kg/km² per year	
	tropical rain forests	seasonal tropical forests and parkland savannas
Fe	600	200
Mn	615	205
Sr	105	35
Ti	97	32
Zn	90	30
Ba	67	22
Cu	24	8.0
Zr	22	7.5
Ni	6.0	2.0
Cr	5.2	1.7
V	4.5	1.5
Pb	3.7	1.2
Co	1.5	0.5
Mo	1.5	0.5
Sn	0.75	0.25
Ga	0.15	0.05
Cd	0.11	0.035
Average ash content, %	4.6	4-5
Overall turnover of ash elements, ton/km² per year	150	50

The concentration of zinc varies accordingly from 120 to $450 \cdot 10^{-4}$%, and that of TiO_2 from 200 to $1800 \cdot 10^{-4}$%.

Table 11.3 compares the contents of trace elements in the ash of grasses and tree (acacia) twigs from the savannas of East Africa. As is seen, heavy metals accumulate preferentially in the grasses, and barium and strontium, in the trees. The strontium concentration tends to increase with aridity. During our expedition in the arid regions of southern Tanzania, we have found strontium in the baobab twig ash at a concentration of about 4500 μg/g; once, the analysis of acacia twigs for Sr gave a concentration three times as high.

The aerial parts of savanna grasses exhibit a high ash content from 6 to 10%. In part, this is due to the presence of minute particles of mineral dust

Table 11.3. Coefficient of Biological Absorption and Concentration of Trace Elements in the Ash of Savanna Grasses and Trees (East Africa)

Element	Element concentration, μg/g		Coefficient of biological absorption, K_b	
	grasses *Gramineae* (6 samples)	acacia twigs (9 samples)	grasses (*Gramineae*)	acacia twigs
Ti	1140	230	0.1	0.03
Mn	1880	943	1.9	0.9
V	59	45	0.3	0.2
Cr	28	12	0.2	0.08
Ni	39	144	0.6	2.0
Co	20	12	0.6	0.4
Cu	85	39	1.5	0.7
Pb	34	21	1.5	0.9
Zn	118	79	1.2	0.8
Mo	57	6	7.1	0.8
Nb	59	18	0.9	0.3
Zr	165	92	0.5	0.3
Ga	36	4	1.6	0.2
Sr	450	3340	3.5	25.7
Ba	440	630	3.0	4.3

which is discernible under a microscope or, occasionally, even with the naked eye. The mineral dust accounts for 2-3% of the weight of absolutely dry matter of the aerial parts of grasses. Apparently, the mineral dust is mainly responsible for elevated concentrations of gallium: this element is poorly taken up by plants, but its content is high enough in the wind-blown finely dispersed clay mineral. However, even with allowance made for the silicate dust content, the sum total of ash elements in savanna grasses is twice as high as that of alpine meadow grasses.

Irrespective of the elemental content of soils and soil-forming rocks, strontium, barium, manganese, zinc, copper, molybdenum, and nickel are elements that are most actively involved in the biological cycle of tropical biocenoses. The value of K_b for these elements is, as a rule, greater than 1. Beryllium, zirconium, titanium, and vanadium are the most reluctant to enter into the biological migration. These general features manifest themselves not in a like manner in various landscapes. The uptake rate for manganese and zinc by the herbaceous vegetation of Kilimanjaro alpine meadow landscapes

situated at higher than 3000 m above the sea level is greater than that by the herbaceous vegetation of light forests and savannas of the Tanganyika Plateau. In turn, the herbaceous vegetation of savannas absorbs more actively copper, nickel, and, especially, molybdenum, with its K_b greater than 7. The relatively high value of K_b for gallium, niobium, and a number of other elements in the savanna grasses may be attributed, as has been noted above, to the thin layer of silicate dust. The trees of a mountainous, humid fogbound Kilimanjaro forest absorb heavy metals (manganese, zinc, copper, lead) more actively as compared to the trees of a dry forest in the Tanganyika Plateau, where strontium is the most actively accumulated element.

The German botanist H. Walter (Walter 1964) turned his attention, not without reason, to the ambiguity of the term "savanna". This term is loosely applied to denote the vast variety of tropical vegetation represented by diverse assemblages of trees, shrubs, and grasses. Ranked among the savannas are clusters of small light forests alternating with open spaces of herbaceous vegetation. Such landscapes are common under the conditions of a good atmospheric humidity and a dry season of not longer than 4 months. On the other hand, arid territories with a dry season lasting for 7-10 months are also regarded as the savannas. Not only trees, but also numerous grasses cannot withstand such severe conditions, and the vegetation in such areas is represented by thorny drought-deciduous shrubs that stay leafless for a larger part of the year thus reducing transpiration. In fact, the term savanna applies to tropical and subtropical forest steppes with a wide range of rainfall from 200-300 mm/year to 1000 mm/year or even more.

To estimate quantitatively the biomass, both produced and shed, of savanna vegetation, one must overcome significant methodical difficulties. This fact underscores the value of the results that have been obtained in a detailed study of the biogeochemistry of a dry savanna in western India (Rodin *et al.* 1977).

The territory of interest, known under the name of Tar desert, is a lowland alluvial plain formed by the Indus. The rainfall for this territory is 200 to 600 mm/year. The vegetation is represented by scattered widely trees (species *Acacia, Prosopis spicigera, Salvadora persica*), shrubs, and grasses (*Gramineae*). The sandy deposits are devoid of trees, which confers the image of a desert on the landscape. The desertification of the territory is a result of human activities. In 326 B.C., when the troops of Alexander the Great came to the Indus, sal forests (*Schorea rubista Gaerth. f.*) thrived in the territory; at present, these forests are non-existent.

The vegetable biomass of a dry savanna is characterized by the data in Table 11.4. One will observe that trees are major contributors to the vegetable biomass (2680 tons per sq. kilometer) of the savanna. As shown by the available results, trees account for 60% of the root mass and for 98% of the aboveground mass of the floral assemblage of the savanna. At the same time, a larger part of

Table 11.4. Biomass and Productivity of Plant Community of Dry Savanna Rajputana (after the Data of Rodin *et al.* 1977)

Biomass components	Biomass		Productivity	
	ton/km^2	%	ton/km^2 year^{-1}	%
Green parts of plants	290	11	290	42
Perennial aerial parts of plants	1060	47	40	2
Roots	1130	42	353	56
Total of biomass	2680	100	680	100

the annual vegetable production is provided by the grasses. In the total biomass annually produced by the floral community, the grasses account for 76% of green organs, and for 83% of roots. It is to be inferred therefore that the herbaceous vegetation plays a major role in the involvement of chemical elements in the biological cycle of a tropical forest steppe (savanna).

Presented in Table 11.5 is the mass distribution of chemical elements in the biological cycle of a dry savanna. An examination of the results allows one to reach the conclusion that the green parts of savanna vegetation accumulate more than a half of the mass of ash elements and nitrogen, and the roots, about 40%. No more than 5% is supplied to the trunk and twigs. In the green organs of plants, the most actively accumulated are nitrogen, potassium, and sulfur (each accounting for 60% or more of its respective mass in the annual production), also phosphorus, calcium, and sodium (57-58%). In the roots, the highest relative accumulation is that of manganese and silicon which are distributed roughly in equal parts in the annual growth of green organs and roots. In the absolute value, at the highest turnover of 4-6 ton/km^2 per year involved in the biological cycle are calcium, potassium, and silicon. The turnover for iron and manganese does not exceed 200-300 kg/km^2 per year.

A remarkable feature of the tropics is the seasonal bog landscape. The surplus of water during the rain seasons leading to the accumulation of water in relief depressions and lowlands is not favorable to the existence of trees, but beneficial for the development of high grasses. The African grass landscapes composed of the genera *Pennisetum, Hypprrhenia, Themeda, Sorghastrum* and others have received the name of grasslands. We are not aware of any evidence on the grassland biomass structure. According to our data, the grassland species

Table 11.5. Mass Distribution of Chemical Elements in the Biological Cycle in the Dry Savanna of Rajputana (Based on the Data of Rodin *et al.* 1977)

Element	Elemental content in biomass, kg/km²	Elemental content in annual production					
		green parts		roots		overall production	
		kg/km²	%	kg/km²	%	kg/km²	%
N	17934	4286	59	2614	36	7208	100
Si	5381	2214	52	2021	48	4248	100
Ca	25625	3422	57	1928	32	5978	100
K	11121	3157	61	1868	36	5204	100
Mg	4869	680	51	540	41	1330	100
P	1219	357	56	268	42	642	100
S	1760	886	72	318	26	1239	100
Al	1937	246	52	180	38	469	100
Fe	1137	164	53	121	39	311	100
Mn	284	101	48	107	51	209	100
Na	952	279	58	195	40	482	100
Cl	1496	516	54	427	45	951	100
Total (except N)	57181	12022	57	5979	38	21063	100

actively accumulate manganese, copper, zinc, strontium, and molybdenum. The value of K_b for the first four of these measures a few units, and for molybdenum, greater than 10.

The fresh-water plants are poor accumulators of trace elements. In particular, the metal ash content in the papyrus (*Cyperus papyrus*), a representative of the riverine plant community of the White Nile, are: titanium and manganese, $100n \cdot 10^{-4}\%$; zinc, barium, and niobium, $10n \cdot 10^{-4}\%$; copper, $n \cdot 10^{-4}\%$.

11.2. Biogeochemical Characterization of Tropical Soils

A characteristic feature of tropical ecogeosystems is the high rate of edaphic biological processes. This may be exemplified by the data we have obtained in our studies on the soils of Central and East Africa. In the rain forests of Africa, the soil surface receives annually 1200-1500 ton/ha of plant remains (by dry weight). Despite the significant amount of shed material, most

of it undergoes rapid degradation owing to the biotic activity of edaphic invertebrates and microorganisms. In the rain forest, a continuous forest litter is practically nonexistent: a thin layer of dead leaves alternates with patches of naked ground. Elements as supplied in the shed material become taken up by the complex root system of multi-storeyed rain forest to reenter the biological cycle.

The unconsolidated covering deposits of tropical land which serve as a mineral substrate for the recent soils consist to a significant extent of severely leached products of ancient weathering; these contain a limited number of elemental forms accessible to plants. The decomposed plant remains are a major source of such forms. The root system of rain forest trees spreads within the subsurface soil 50-70 cm deep, which is dictated by the necessity of taking up the nutritional mineral elements from degraded shed materials. In the forests of the Amazonian basin, the tree roots lie at a still smaller depth of 10-20 cm (Walter 1964).

The microbiological transformation of dead organic matter in the rain forest soils leads to readily soluble fulvic acids. Their concentration is 5-6 times higher than that of humic acids. In soils overlying well washed-out products of weathering of quartz-containing crystalline rocks, the pH of humus horizon is about 5. The upper profile of such soils is severely leached. In a rain forest confined to a volcanic region and grown on the soil overlying the weathered products of young volcanic rocks rich in alkalies and calcium, a significant part of humic acids become neutralized and condense into larger, less soluble compounds. The resulting effect is that 6% or even more of humus accumulates in the upper soil profile has a pH close to 6; still, fulvic acids remain in excess over humic acids.

In regions with a short dry season, of wide occurrence are light tropical forests and parkland savannas. The soils in such landscapes give a neutral reaction and are subject to periodic wash-out during the rainy seasons. The rank grass cover is favorable to the formation of sward and humus horizons. The situation is quite different in a territory with prolonged dry seasons at a rainfall of 600 to 400 mm per year or even less. Under such widespread conditions arid savannas, dry deciduous forests, dense shrubbery are found. The soil wash-out is never complete; the microbiological activity is suppressed in dry seasons, and the vegetation coverage is less than 50%. In the soils of dry savannas and shrublands, the humus content is rather low; the soils give an alkaline reaction with pH about 7-8.

A characteristic feature of the tropical land is the clearly distinguished geochemical provinciality of the soil cover. This is due to a number of reasons. First, a substantial part of tropical land is destitute of a deep cover of allochthonous glacio-loessal deposits that are widespread in the territory of boreal and subboreal zones. The tropical soils have been formed mostly on redeposited products of weathering that suffered a small displacement. Second,

the tropical continents have originated as fragments of the ancient supercontinent Gondwana whose surface during the last half-billion years evaded contact with the World's ocean. The resultant effect was that the soils have inherited the compositionally variable specificity of the exposed soil-underlying rocks. Consequently, given identical climatic conditions, the plants of various regions sequester different amounts of trace elements.

By way of example, we wish to refer to our data on the content of trace elements in monotypic soils of the savannas in Uganda and northern Tanzania. The Ugandian soils overlay the Precambrian crystalline rocks; the soils of Tanzania are confined to the outcrop area of the Cenozoic volcanic rocks of the East-African Rift. These soils are enriched in the elements present in elevated concentrations in the alkali basalts and phonolites of the East-African Rift: zirconium, titanium, beryllium, niobium, strontium, and a number of other elements.

The data listed in Table 11.6 show that the savanna soils of Tanzania contain niobium 11 times, beryllium and molybdenum 6 times, and titanium and zirconium 4 times as high as compared to the respective crustal abundance of these metals. In turn, the chromium concentration in the savanna soils of Uganda is seven times its crustal abundance, and the copper concentration, five times. Such a large difference in soil element concentrations is reflected in the proportion of these elements involved in the biological cycles of the two neighbouring savanna regions of East Africa.

Biogeochemical processes occurring in the soil are intimately linked to the migration of chemical elements in the surface waters of tropical land. Their geochemistry has been little studied; still, the available evidence indicate that the concentration of many elements in tropical rivers is lower than the respective average concentration in the World's rivers. This may be attributed to two reasons. First, the phytocenoses of tropical forests put a strict sequestration on the needed chemical elements and are reluctant to leave them from biological cycling. Second, certain elements, especially heavy metals, are more tightly bound in the red color products of weathering and in their overlying soils than in the Quaternary deposits from which the soils of boreal and subboreal belts originated.

As has been established, the concentration of salts and such elements as boron, fluorine, and strontium in the waters of tropical rivers tends to increase during a dry season. The studies that were carried out by Obukhov (1968) in Burma have shown that in the rainy seasons the concentration of metals shows a slight, but reliably identifiable increase. One may presume that this effect is due not only to the wash-out of soluble metal compounds, but also to an enhanced microbiological activity in the soil. Significant amounts of metals in the form of complexes with soluble fulvic acids are carried over by tropical rivers.

Table 11.6. Concentrations of Trace Elements in Savanna Soils of Two Regions in East Africa (Dobrovolsky 1975)

Elements	Concentration in humus hori-zon, μg/g		Clarke of concentration	
	Uganda (44 samples)	Tanzania (12 samples)	Uganda	Tanzania
Ti	5820	14900	1.8	4.5
Mn	1520	2140	2.2	3.1
V	153	271	2.0	3.6
Cr	234	160	6.9	4.7
Ni	75	93	2.9	3.6
Co	48	70	6.6	9.6
Cu	105	72	4.7	3.3
Pb	52	35	3.2	2.2
Zn	125	190	2.5	3.7
Mo	5	8	3.8	6.2
Be	6	16	2.4	6.4
Sc	24	16	2.2	1.5
Y	58	64	1.6	1.8
La	85	95	1.8	2.1
Nb	59	224	2.9	11.5
Zr	215	670	1.3	3.9
Ga	16	20	0.8	1.1
Cr	129	510	0.6	2.2
Ba	274	590	0.4	0.9

Most of the chemical elements migrate as suspensions. The river stream suspensions are mainly composed of products supplied by the soil surface run-off. Most of these products actively washed-off during rainy seasons never reach the river valley and become retained in relief depressions. Simultaneously, the groundwater level in relief depressions rises, or a seasonal perched-water horizon is formed. In the regions of seasonal water-logging, vertisols are formed which are gray and black compacted tropical soils overgrown by the previously mentioned grassland communities. The seasonal bog landscapes provide conditions for the accumulation of chemical elements that migrate from the elevated surrounding territory. For this reason, the soils and plants develop higher concentrations of trace elements leading occasionally to the occurrence of biogeochemical anomalies.

11.3. The Mangrove Biogeochemistry

The biogeochemistry of mangroves deserves special consideration. The mangrove forests are a vegetational type characteristic of the tropical land coastline. Mangrove forests grow in coastal strips periodically flooded during the diurnal or the big (syzygial) tides and constitute thus a transition *sui generis* from subaquatic marine ecosystems to terrestrial plant communities. The mangrove vegetation, by virtue of its living conditions, is indifferent to rainfall variations, but is very sensitive to low temperature. Although the mangroves are a vegetational type characteristic of the tropic belt, they spread, depending on the local temperature conditions, as far as 32° N (the Bermuda Islands) and 44° S (Chatham). Their floristic composition is the most diversified in the Indo-West-Pacific region (islands and coastline), where the occurrence of 44 varieties have been reported (Machae, 1968). In the Atlantic, the mangroves are especially widespread in the Caribbean region. The chemical composition of mangrove vegetation and the distribution of strontium and heavy metals in the soils of islands of the Caribbean region and the Indian Ocean have recently been studied (Dobrovolsky 1989).

Mangrove forests thrive either on carbonate sands, aleuritic and clayey silts in lagoons and shallow bays, or on the surface of compact cavernous reef limestones. Less frequently, single mangrove trees or their small clusters grow on coastal quartz sands derived from weatherworn crystalline rocks. Among the mangrove vegetation are distinguished red mangroves of the genus *Rhizophora*, black mangroves of the genus *Avicennia*, and white mangroves with the predominance of the genus *Laguncularia*. In the atolls of the Indian Ocean, the community of mangrove trees becomes augmented with shrubs of the genus *Pemphis*, commonly residents of the compact reef limestone ledges at the coastal strip.

The composition of mangrove vegetation thriving on coral limestones and sands is of special interest. Compositionally, the leaves of mangrove trees as compared to the leaves of tropical forest trees contain much more magnesium, sulfate sulfur, chlorine and appreciably less potassium and silicon, these two elements, in addition to calcium, being major ash elements of the tropical forest litter. It is noteworthy, that the aluminum content in mangrove leaves is 3-4 times that of silicon. The sum total of ash elements in mangrove tree leaves accounts for 11 to 23% of the vegetable material (by dry weight). This is significantly higher than the ash content of terrestrial plants growing on analogous limestone soils which commonly is 5-6%. This difference in ash elements should be attributed to the fact that the terrestrial island plants require fresh underground or rain waters, whereas the mangrove trees are adapted to saline seawater.

The distinction between terrestrial and mangrove vegetation is also manifest in the content of individual components. Most of mineral components of the vegetative and deciduous organs of mangrove trees (leaves and partly twigs) are accounted for by calcium and magnesium whose content is higher than that in the terrestrial island plants. The contents of sodium, chlorine, and sulfate sulfur roughly compare with those of terrestrial plants; as distinct, silicon, iron, and phosphorus are present in significantly smaller amounts.

Despite the substantial concentrational variation of trace elements in the vegetative organs of mangrove trees of the same species, one will note certain features typical of the mangrove vegetation as a whole. A common biogeochemical property shared by the mangroves is the low content of heavy metals, and the high content of thalassophilic elements, in particular, strontium. The relevant examples are given in Table 11.7.

The mangroves constitute one of the most productive phytocenoses. Their biomass is in excess of 100 ton/ha of dry vegetable matter. The annual production of the Puerto Rico mangrove forests amounts to 10-30 ton/ha of dry vegetable matter, the leaf litter production of 8-15 ton/ha included (Scholander *et al.* 1965).

The mangrove vegetation is finely reflective of any change in the environmental metal content. The data in Table 11.7 show that the leaves and twigs of mangrove trees, residents of the tidal zone of silicate (magmatic) islands, contain more iron than 300 μg/g (on an ash-weight basis) and manganese more than 50 μg/g, whereas in analogous species thriving in the lagoons of coral islands, the concentration of iron is lower than 200 μg/g and of manganese, lower than 40 μg/g. The concentrational distribution for strontium is exaclty opposite: the content of this element in the leaves of mangrove trees of coral islands is higher than 1000 μg/g (by ash weight) and in those of magmatic islands, lower than this value.

The available data on the ash content of heavy metals in the vegetative organs of mangrove vegetation allow, in a first approximation, to estimate the annual turnover of heavy metals in the mangrove phytocenoses. The least ash yield, 10-12%, is typical of the rhizophores that take the lead in the mangrove communities. Taking into account the fact that other mangrove trees and shrubs exhibit a higher ash yield, one may accept the mean ash content for the vegetative organs of mangrove plants to be 15% (an average of 10 and 20%) by dry weight of vegetable matter.

The sum total of ash elements involved in the biological cycle of mangrove phytocenoses ranges from 0.8 to 3 ton/ha per year, on the average about 1.9 ton/ha or 190 ton/km^2 per year, as estimated by the leaf litter production (Pool *et al.* 1975) and the sum total of ash elements (Dobrovolsky 1989). Based on the available data, one can determine the annual turnover of heavy metals and strontium in mangrove vegetation. The pertinent results are summarized

Table 11.7. Concentration of Heavy Metals and Strontium in Mangrove Vegetation of Islands in the Indian Ocean

Plant and island	Chemical element and concentration, μg/g (by ash weight)						
	Fe	Mn	Zn	Cu	Pb	Ni	Sr
Mangroves of coral islands							
Rhizophora mucronata (leaves and twigs)							
North Poivre	126.3	36.8	28.4	18.4	0.0	5.0	1200.0
South Poivre	162.5	25.0	50.0	35.0	8.8	8.1	2000.0
North Farquhar (leaves)	86.6	13.8	42.0	15.8	6.9	6.0	1333.0
North Farquhar (twigs)	76.9	32.0	60.0	36.0	6.4	2.5	3200.0
Mangroves of silicate islands							
Rhizophora mucronata (leaves and twigs)							
Silhouette	357.1	71.4	45.3	10.7	0.7	3.8	793.0
Bruguiera gymnorhiza (leaves and twigs)							
Silhouette	437.5	306.2	70.0	20.6	2.5	0.9	963.0

12 Specific Features in the Biogeochemistry of Sea Islands

The ocean exerts a potent and diversified influence on the terrestrial biogeochemical processes. The effect of sea basins on the climatic conditions of vast territories is an important factor in the distribution of plant formations with different biomass and productivity and, consequently, in the regulation of the mass of the World's land living matter. Currently, the researchers become increasingly aware of a role of the ocean as the source of chemical elements and compounds delivered to the ecogeochemical systems of land. The present Chapter is concerned with the effect of sea basins on land territories and is, in a sense, complementary to Section 3.3 where the global aspects of mass exchange between ocean and land have been discussed.

12.1. Salt Mass Transfer and Role of Bird Colonies

The most apparent geochemical effect of sea on land is the transport of sea salts onto the coastal territory. According to the data of Eriksson (1958) on the northern seacoast of the Mexican Gulf, about 3000 tons of salt is annually carried over across a 1 km stretch of shoreline at the average annual wind velocity of 3 m/s. Under definite conditions, the sea salt precipitation onto the land is quite significant. As has been reported by Borovsky *et al* (1974), at the western point of the Mangyshlak peninsula 1.5 km distant from the Caspian Sea shoreline, about 667 kg of salt per hectare was precipitated during a period of 69 days. At the same time, numerous data provide evidence that, in the inland territory, the soluble salt concentration in rainfall decreases rapidly away from the shoreline. Studies by Mikhalenok (1989) in the East Crimea seacost have shown that the high sea-salt ion content in the inland rainfall does not reach beyond a distance of 10-12 km. Apparently, the zone of oceanic geochemical effect on land is incomparably narrower than the hydrothermal area whose intracontinental influence reaches into thousands of kilometers. The rainfall concentration of salt elements decreases very rapidly, apparently, as a nonlinear function of the seacoast distance. Consequently, in the continent the sea-salt mass transport is confined to a relatively narrow coast strip and leaves the intracontinental territory essentially unaffected. In small islands,

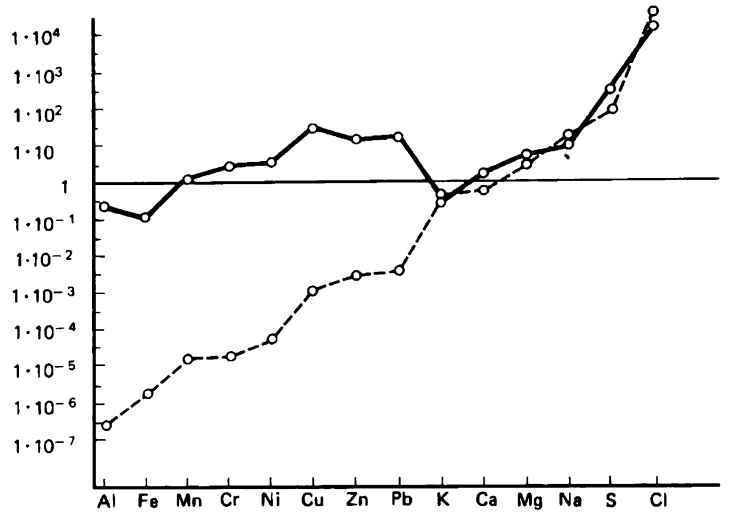


Fig. 25. Clarkes of concentration of chemical elements contained in the salt part of oceanic water (dashed line) and in the pelagic aerosols of the World's ocean (solid line). Noted are a close correspondence for potassium, calcium, magnesium, sodium, sulfate sulfur, chlorine, and a large difference of 3-to-5 orders of magnitude for heavy metals

whose territory and biota are exposed to oceanic influence, the situation is quite distinct. For this reason, the biogeochemical mass-exchange processes in islands exhibit a number of specific features.

Of exceptional importance for the vegetation salt balance are both the salt supply to the soil surface and the uptake of salts by the plants. Detailed studies of sea-salt distribution in the littoral vegetation have been carried out in the Solovetskie Ostrova situated at 65° N in the White Sea (Dobrovolsky and Kozarenko 1989). The chosen sampling site was a wide shallow coast strip with intergrading ecotones exposed to a high (4-5 m) tidal flood.

The littoral is a habitat for thickly growing varieties of algae (*Fucus vesiculosus*, *Laminaria Saccharina*, *Enteromorpha intestinalis*, *Anfeltia plicata*) and single algal specimens and halophytes (for example, *Aster tripolium*, *Plantago Schrencii*, *Atryplex nudicalis*, *Leymis arenarium*, *Lathyrus alenticus*, and others). The intertidal zone upgrades into a broad beach interspersed with low ridges of decayed algae and shallow salt marshes. A step 0.3-0.4 m high is the border line between the beach and a narrow strip of coastal tundra which merges into a shrub-grown territory. Further inland, it becomes replaced by a broad belt

of birch dwarf forest, and this, by a northern taiga which occupies the central part of the larger islands of the Solovetsky archipelago.

The ash content of the plants thriving in the intertidal zone and the beach varies from 4 to 9% by dry weight. The highest ash content, 12.9%, has been recorded in the sea aster (*Aster tripolium*), a typical halophyte of the Solovetskie Ostrova. To be noted for comparison, the ash content of local algae is much higher reaching 20-30%. There has been outlined a general trend in the concentrational distribution of major salt-forming cations in the plants: moving inland, the concentration of sodium and magnesium decreases, whereas that of potassium and calcium remains essentially unchanged (see Table 12.1). This trend is reflected in the curves in Fig. 25 showing that the Na/K and Mg/Ca ratios for inland plants decrease roughly by a factor of 10 in comparison to those for the species of the tidal zone.

The elemental analysis of samples taken from the widespread plants: leaves of the birch (*Betula tortuosa*), twigs and leaves of the bog bilberry (*Vaccinium uliginosum*), and lichens (*Parmelia*) has provided evidence that in plants with atmospheric nutrition (lichens), a sharp concentrational decline of all trace elements is clearly observed at a distance of about 2 km from the shoreline; this drop typically occurs within a narrow interval of 10-20 m along the sampling transect. In plants with predominant edaphic nutrition, the concentrational decrease of potassium and calcium as supplied from the atmosphere is undistinguishable from the supply of these elements from the soil, whereas with sodium and magnesium one will observe a tendency to concentrational decrease, which shows up more clearly in shrubs than in trees (especially for sodium).

The atmospheric precipitation of salts and their accumulation in plants produce an effect on the composition of coastal soils. Moving inland from the coast, the concentration of exchangeable cations of sodium and magnesium decreases, with a concomitant compositional change of organic matter of the soil.

The effect of air-borne sea salts is also clearly reflected in the composition of the tropical island vegetation. Here a characteristic feature is the high concentration of thalassophilic chemical elements such as magnesium, sodium, chlorine, sulfate sulfur, and strontium. These elements are contained in the plants growing in islands of tropical seas and oceans in concentrations appreciably higher over those average for terrestrial plants, but, nonetheless, lower than for sea algae. The calcium concentration is also high but, because of the greater increase in magnesium, the Ca/Mg ratio in the insular vegetation is lower than in the continental. For the Na/K ratio, the exact opposite holds true.

One will observe, against the background of general trends, that the systematic position of plants and ecological conditions bear relevance to the

Table 12.1. Concentration of Major Salt-Forming Cations in Plants of the Solovetskie Ostrova as a Function of Distance from Seacoast

Plant	Distance from seacoast, m	Ash yield, %	Elemental content, % by dry weight			
			Na	K	Mg	Ca
Betula tortuosa	5	3.6	0.057	0.58	0.84	1.27
	10	5.2	0.088	0.72	1.10	1.72
	25	4.6	0.032	0.76	0.86	1.49
	50	4.7	0.023	0.60	0.28	1.24
	200	4.6	0.029	0.71	0.88	1.88
	2000	4.6	0.050	0.83	0.04	1.45
Vaccinium uliginosum	10	3.6	0.230	0.68	0.42	0.59
	25	4.1	0.140	0.69	0.48	0.71
	50	3.6	0.100	0.60	0.24	0.59
	100	4.0	0.100	0.70	0.29	0.56
	200	3.7	0.090	0.56	0.30	0.66
Parmelia	10	3.6	0.100	0.67	0.45	1.04
	25	2.3	0.047	0.17	0.20	0.46
	50	2.7	0.023	0.32	0.47	0.78
	100	1.6	0.021	0.12	0.13	0.30
	200	2.7	0.037	0.21	0.19	0.89
	2000	2.4	0.027	0.19	0.16	0.42

compositional specificity in plants. Typically, grasses exhibit the highest level of silica. A maximum of sulfates has been found in the shrubs (in pemphis). The available data also reveal that the contents and proportions of certain ash elements are unquestionably dependent on the ecological situation.

The salt transport is an obvious, but not the only one, factor in the geochemical action of ocean on land. The salts are supplied to the troposphere mainly through entrainment of seawater dust by the wind. Along with the mechanical entrapment and transport of soluble salts, a selective supply of chemical elements and compounds from the ocean takes place. Besides, there arise, at the land-ocean interface, specific food chains that tie the biogeochemical activities of marine and terrestrial organisms into a common system of biological cycles. Finally, the direct interference of sea water in the tidal zone or in periodically flooded places favor the emergence of unique thalassomorphic ecogeosystems. A typical example is the mangrove vegetation that has been dealt with in the foregoing chapter.

The soil of coral islands-atolls may serve for a perfect object in studying the geochemical effect of the ocean on the biogeochemistry of terrestrial landscapes. The atoll phytocenoses, isolated from the continents by thousands of kilometers of water space, have formed on a geochemically pure carbonate substrate that was allowed to pass through the biological filters of reef-forming organisms; still, they are never short of chemical elements needed for the development of tropical vegetation.

Islands composed of magmatic or sedimentary rocks are less convenient objects to study. Chemical elements (heavy metals included) contained in the parent rocks are inherited by the soils and, supplied to the plants, create a background against which the incessant flux of metal ions from the atmosphere becomes indiscernible.

The climatic conditions in atolls are specified by the occurrence of the atolls in the tropic belt of the World's ocean. The average yearly temperature is maintained at a steady level of 27-28 °C, the rainfall is 1500-3500 mm per year, under variable dry and rainy seasons from island to island. The evaporation is rather high reaching 1200-1500 mm per year.

By morphology and structure, two groups of atolls are distinguished. The first group are low or sandy islands, with their height not exceeding 3-4 m above the high-tide level. They represent accumulations of coral sand or clastic fragments of larger size rested on a compact reef basement. The second group includes high, or elevated atolls. They are composed of compact reef limestone and most commonly have several abrasion terraces.

The hydrologic regimen of low and high islands, despite their identical climatic conditions, is drastically different. The low islands are subject to a systematic soil washing. The rain waters, on their passing through the coral sand, form an upper layer over the heavier and more dense sea water impregnating the island basement. The high atolls are heavily karstic, the rainfall takes little time for its transit through the ground riddled with numerous caverns, which prevents the formation of a suspended horizon of fresh water.

Dissimilar hydrologic conditions in atolls of different type exert an influence on the floristic composition. The primary vegetation of low atolls is almost completely replaced by forests of coconut palm (*Cocos nucifera*), partly of native origin, partly planted by man. The palm forests are spaced apart from the tidal zone by a narrow strip of shrubbery of the genera *Scaevola* and *Tournefortia* interspaced in places by single specimens of *Calophyllum* with a spreading and dense crown. Typical of the coastal strip of atolls in the Pacific is the genus *Pandanus*. The lowermost storey of a palm forest is represented by a fragmentary surficial cover of sod-forming grasses of the genera *Kyllinga*, *Stenotaphrum*, *Briophyllum*, *Tridax*, and others adjoined in moist places by ferns (*Nephrolepis*, *Polypedium*, and others). Encountered in the palm forest are arboreal species, singly or in groups, such as *Casuarina*, *Hernandia*, *Calophyllum*,

Terminalia, *Artocarpus*, and others. In the lagoonal areas awash at low tide, mangrove swamps are present composed mainly of the genera *Avicennia* and *Rhizophora*, with an occasional occurrence of *Laguncularia*.

The vegetation of high atolls has an entirely different floristic composition. Here, owing to an extensive karstification, the lack of moisture is felt even at abundant annual rainfall. Dry seasons of more or less prolonged duration lead to still more severe conditions. Predominant on the karstic surface of reef limestone are xerophytic shrubs of the genera *Pemphis acidula*, *Suriana*, *Euphorbia*, *Thespesia*. There occur also single specimens of agaves, ficuses, and aloes. The grass cover is fragmentary, with the prevalence of low-growing species *Gramineae* (*Stenotaphrum*, *Eragrostis*, and others), sedges, and, in places, tufts of *Plumbago aphylla*.

The diversity and large biomass of tropical insular vegetation are clearly at variance with the chemical composition of the carbonate substrate. The deficit in phosphorus, potassium, and heavy metals in the soil-forming rocks of coral islands should have created insurmountable difficulties for plant development. Still, both the biomass and productivity of atollic biocenoses are close to those of some of the widespread phytocenoses of tropical land. It is to be inferred, therefore, that the deficit of nutritional mineral elements in the soil-forming rocks must be replenished from other sources.

A specific source of chemical elements indispensable for the normal development of island vegetation is the bird community. The role of bird colonies, quite modest under continental conditions, becomes an important factor in the biogeochemical cycles of oceanic islands and, occasionally, coastal regions. The bird colonies play a specifically important role in the phosphorus cycle. Findings of the recent years have shown convincingly that precisely phosphorus, rather than nitrogen, is the limiting factor for the development of living matter of the World's ocean. No less important is the role of phosphorus in the geochemistry of insular landscapes.

The atmospheric supply of phosphorus to the surface of islands is 0.9-1.0 kg/ha per year, including 0.1-0.2 kg/ha in soluble form in rainfall (Bezborodov *et al.* 1984). Along with this, significant amounts of phosphorus are accumulated owing to massive colonies of birds. Observations in the Cousin island making part of the Seychelles have shown that up to 0.9 tons per hectare of organic matter, mostly bird droppings, is stored at bird colony sites (Brooks 1983).

The bird droppings are a mixture of organic compounds, uric acid and its salts, also salts of mineral acids. All these species are reactive and, when dissolved in rain water, enter into an active interaction with reef limestone, with the resulting formation of calcium phosphates, the so-called atoll phosphates. The soluble phosphorus compounds become washed down into the ocean and, entering into the food chains of the reef community, maintain its uncommonly high biogenic activity. The latter, in turn, provides a nutritive base for birds.

Thus, the status of a coral reef as an oasis in the ocean is to a significant extent determined by the biogeochemical phosphorus cycle which, in large measure, is linked with the biogenic activity of bird colonies.

Guano contains, apart from phosphorus, a large number of trace elements. For this reason, phosphatized limestones contain larger amounts of some metals than pure reef limestones and atoll sands that escaped biogenic phosphatization. With phosphorus content increasing, the concentration of iron, zinc, and cadmium increases, whereas the concentration of strontium decreases because of its leaching out of reef limestone by acidic solutions.

The avian factor in the biogeochemistry of insular ecogeosystems is conspicuously manifest also in islands frequented by birds in other climatic zones. It will suffice to recall the famous bird colonies ("bird bazaars") in the islands of Arctic sea basins.

12.2 Atmospheric Delivery of Heavy Metals to the Ecogeosystems of Islands

An important factor in the biogeochemistry of insular vegetation is the atmospheric supply of certain chemical elements. This is clearly seen in studying the atoll biogeochemistry.

The atoll reefs have arisen from the activity of lime-secreting shallow-water organisms, mostly coral polyps and calciferous algae. A characteristic feature of calcium-carbonate atoll accumulations is their high geochemical purity. The metal contents in atoll carbonates are 10 to 100 times smaller than their respective lithospheric crustal abundances. The only exception among the trace elements is strontium whose crustal abundance is much inferior.

Table 12.2 lists the concentration of heavy metals and strontium in the soil-forming rocks of oceanic islands. One will observe that the concentration of heavy metals in silicate substrates is appreciably higher than that in coral limestones. The exactly opposite holds true for strontium whose concentration in coral limestones and sands is higher by three orders of magnitude as compared to the soil-forming rocks of magmatic islands. However, the metal proportions in the mineral substrates of islands do not parallel those in the vegetation.

Summarized in Table 12.2 are also data on the heavy metal concentrations in the vegetation of atolls in the western Indian Ocean and in the vegetation of the Seychelles built up of magmatic rocks. The available evidence allows one to infer that compositionally the vegetation of oceanic islands exhibits trends typical of terrestrial vegetation; still, one will notice a lower concentration of some heavy metals and the accumulation of thalassophilic elements, in

Table 12.2. Concentration of Heavy Metals and Strontium in Soil-Forming Rocks and Vegetation of Islands in the Indian Ocean

Elements	Granitic islands			Coral islands		
	M, μg/g	s, μg/g	V, %	M, μg/g	s, μg/g	V, %
			Soil-forming rocks			
Fe	82600.0	41000.0	49	30.0	17.0	57
Mn	970.0	430.0	44	3.2	1.5	47
Zn	100.0	40.0	40	8.9	2.5	28
Cu	17.0	13.0	76	1.7	1.2	70
Pb	35.0	17.0	48	0.11	0.1	91
Ni	3.1	2.0	64	0.4	0.2	50
Sr	0.6	—	—	5360.0	2239.0	42
			Vegetation			
Fe	969.7	696.1	72	309.6	250.4	81
Mn	1489.3	1498.3	101	46.7	45.8	100
Zn	198.9	100.4	51	162.9	155.4	95
Cu	62.6	34.5	55	31.8	15.3	49
Pb	8.8	9.5	108	4.6	3.9	85
Ni	15.5	10.6	68	7.7	3.8	49
Sr	500.9	302.0	60	2238.9	2187.7	98

Note: M is the arithmetic mean; σ is the standard deviation; V is the coefficient of variation

particular, strontium. As is seen in Table 12.2, the heavy metal contents in magmatic rocks and the carbonate substrate of atolls differ by tens and hundreds of times. In contrast, the concentration of most metals is but slightly lower in the vegetation of atolls than in that of magmatic-rock islands. Thus, the atoll vegetation, viewed vis-à-vis the coral substrate, is an active geochemical accumulator of metals.

The coefficients of biological absorption of metals for the vegetation of silicate islands are close to or somewhat lower than the K_b values for the continental vegetation. The coefficients of biological absorption of heavy metals as estimated with respect to the metal concentrations in the atoll substrate are greater than 10. In view of the negligible metal content of reef carbonates and the active uptake of metals by vegetation, one might presume that the vegetation could be a potent factor in the rapid destruction of low atolls rising but slightly above the sea level. Since this is not the case, one may hypothesize that the heavy metals are supplied from sources other than the reef limestones.

An entirely different is the case with the strontium uptake. The concentration of this element in coral limestones and sands is largely in excess of its requirement by plants. For this reason, the coefficient for biological absorption of strontium by the atoll vegetation is smaller than 1 despite the fact that the absolute concentration of this element is significantly higher than that in the continental vegetation.

There is good reason to believe that the chemical elements occurring in the oceanic insular vegetation are being obtained from a variety of sources. Indicative of this are systematic concentrational differences for certain metals recorded not only in the terrestrial vegetation of coral and magmatic islands, but also in the mangroves growing in the atoll and reef fringes of magmatic islands. Certain mangrove species, for example, *Rhyzophora mucronata* or *Bruguiera gymnorhiza*, inhabitants of the reefs fringing the granitic Seychelles are much higher in iron and manganese than their congeners exposed to analogous ecological conditions in atolls. Apparently, the reef mangroves take up soluble iron and manganese compounds from the littoral sea waters into which these metals are found as components of the rain run-off from the granitic islands. Most probably, this is a major reason for the elevated concentration of iron and, especially, of manganese in the vegetation of magmatic-rock islands. In coral limestones, these metals are less abundant and their concentration is lower in the atoll vegetation.

At the same time, the concentration of zinc, copper, lead, and nickel in the terrestrial vegetation of granitic islands is quite close to that in the mangroves of the neighbouring atolls and reefs. This gives us reason to believe that these metals are delivered to the plants not from rocks, but from a source common to both granitic and coral islands. Such a source of metals for the oceanic insular vegetation can be only atmospheric precipitation.

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The available evidence suggests presuming that the heavy metal content in oceanic rainfall is high enough to provide the appropriate metal concentrations in the atoll vegetation. Our estimates, based mainly on the data of Bezborodov *et al.* (1984) and Chester *et al.* (1974) have given the following amounts of heavy metals precipitated annually over the islands of the western Indian Ocean:

Elements	Supplied in rainfall (soluble forms), kg/km²	Supplied in dry fall-out, kg/km²
Iron	3-9	90-108
Manganese	6-18	9-16
Copper	3-9	0.3-0.6
Zinc	7-21	1.4-1.8
Lead	6-18	0.4-0.7
Nickel	1.5-4.5	0.1-0.2

The origination of air-borne heavy metals in the oceanic troposphere poses a very intricate problem. The carriers for metals can be continental dust, volcanic ejecta, sea-water dust, and oceanic evaporates. As a first approximation (Sugawara 1961), one may attempt to solve this problem by comparing the elemental proportions in oceanic aerosols with those in sea water and in the upper "granitic" layer of the continental crust. In estimating the mass distribution of elements between ocean and troposphere, the common practice is to use values normalized on a Na basis.

In Table 12.3 normalized ratios are given for a number of elements in aerosols, sea water, and granitic continental layer. One will observe, with reference to column 2 in Table 12.3 that, in the composition of oceanic aerosols, the major sea-salt elements (calcium, magnesium) remain in close proportion relative to sodium. Apparently, these elements are supplied as aerosol components through mechanical entrainment of sea-water dust with the wind. The mechanism for supply of heavy metals appears to be quite different, since the aerosols are highly (thousand-fold) enriched in metals (relative to Na) as compared to the sea water.

The comparison of the concentrations of a chemical element in the sea salt and in the oceanic aerosol relative to the abundance of this element in the granitic crustal layer is quite revealing (Dobrovolsky 1988). The relevant data obtained on the Indian Ocean aerosols are given in Fig. 25. As is clearly seen, the relative contents of thalassophilic elements (Cl, S, Na, Mg, and others) in oceanic salts and aerosols are very close, and the respective points in the graph are nearly coincident. At the same time, the relative concentrations for heavy metals differ by a few orders of magnitude.

In estimating the elemental redistribution in reference to the upper layer of continental crust, the relative contents are commonly normalized on an iron

Table 12.3. Relative Contents of Chemical Elements in Aerosols (Indian Ocean Basin), Sea Water, and Granitic Layer of Continental Crust

Elements	Aerosol: ocean	Ocean: granitic layer	Aerosol: granitic layer	Clay deposits: granitic layer
	relative to Na		relative to Fe	
Na	1.0	$55 \cdot 10^5$	10	0.33
Mg	1.9	$11 \cdot 10^5$	3.8	0.98
Ca	3.4	$17 \cdot 10^3$	1.1	0.66
Co	$46.4 \cdot 10^3$	44	4.0	2.0
Ni	$7.8 \cdot 10^3$	200	3.0	2.0
Cu	$9.6 \cdot 10^3$	460	25.0	1.6
Zn	$5.4 \cdot 10^3$	1160	11.6	1.5
Pb	$92.0 \cdot 10^3$	68	4.0	0.96
Fe	$532.0 \cdot 10^3$	1.0	1.0	1.0

basis. As columns 3 and 4 in Table 12.3 show, the elemental proportions for the World's ocean water and oceanic aerosol (with reference to the granitic crustal layer) differ markedly.

The finely-dispersed continental dust with particles less than 1-2 microns affects the metal content in coastal oceanic aerosols. One will also observe a difference in the metal proportions for oceanic aerosols and clay deposits (columns 4 and 5 in Table 12.3). It is to be inferred therefore that the high heavy metal content (relative to iron) is a feature that compositionally distinguishes the pelagic (open-sea) aerosols of the Indian Ocean from both the sea salt and the continental dust.

Researchers who studied the composition of oceanic aerosols (Vilensky *et al.* 1976; Chester *et al.* 1974) hypothesized that the fractionation of chemical elements and the enrichment in heavy metals might occur at the ocean-troposphere interface. The estimates that have been presented above lend support to this hypothesis. The effect appears to be to a large extent associated with biogeochemical processes, mainly biomethylation.

By virtue of the fact that the migration of chemical elements is a pivotal link between the terrestrial and aqueous ecosystems, the next important task is to assess quantitatively the migratory masses. Regrettably, at present we are unable to give a complete picture of the global cycle of the atoll community and must, perforce, focus on its separate parts only.

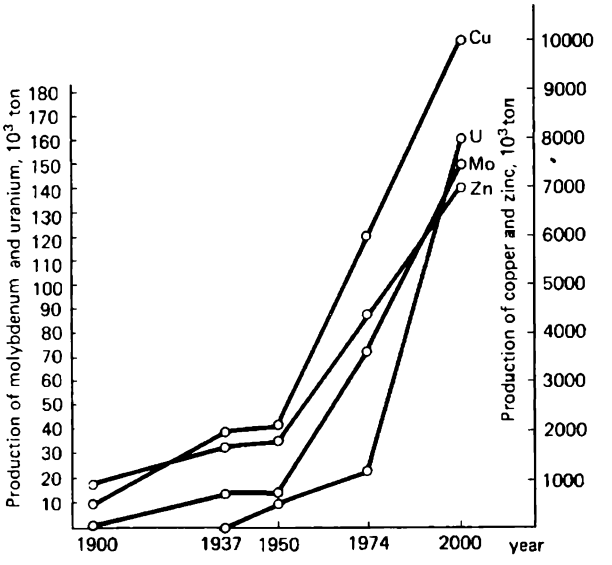

Fig. 26. The rate of metal production in the 20th century

The reef-forming atoll communities, along with the coral islands of other types, represent one of the most productive marine ecosystems. They are often pictured, not without reason, as a sort of cases lost in the desolate expanses of the ocean. For example, according to the data of Odum (1975), the reef communities in the Enevetok atoll are 120 times more productive than their neighbouring communities in the open ocean. The contrast is still more striking if one refers to the average productivity of the tropical belt of the Pacific. This effect of exceptionally high biological productivity against the background of an oligotrophic environment has received the name of "major paradox of the Coral reef" in the ecological literature.

The biomass of the coral's soft body is not large, ranging from 50 to 100 g/m^2 (on a carbon basis), which amounts to 1-2 ton/ha of dry organic matter; still, higher values have also been reported. The productivity of a reef community is disproportionately high to its biomass. The average productivity of a coral polyp community is 4 g/m^2 per day (Preobrazhensky 1986). Consequently, the annual productivity is 1460 g/m^2 of carbon, or about 29 ton/ha of dry organic matter. This is 3-4 orders of magnitude higher than the average productivity of the World's ocean tropical belt (Dobrodeyev *et al.* 1976) and higher than the productivity of a tropical rain forest.

No data on the biomass and its dynamics for the terrestrial vegetation of coral islands are currently available. It may be presumed, by analogy with the

light (deciduous) tropical forests, that the annual growth of atoll vegetation falls within the range of 5 to 10 ton/ha, which is 3-5 times less than the productivity of subaquatic reef biocenoses. Given the average ash yield of 5% for terrestrial vegetation, the annual turnover of ash compounds amounts to 250-500 kg/ha. The involvement of metals in the annual cycle can be approximately characterized by the following estimates (in mg/m^2): iron, 10-15; zinc, n; copper, about 1; and manganese, nickel, lead, $0.1n$. These estimates are commensurate with those for metals supplied to the island surface in rainfall.

The biological cycling of chemical elements in the island landscapes is irrevocably linked to the processes occurring in the soil. The specificity of atoll soils arises from the fact that compositionally they are formed owing to the supply of chemical elements from the outside, rather than at the expense of the soil-forming rock components. The elements, stored in the deciduous plant organs, are delivered to the soil to undergo a variety of complex transformations. The participants of these transformations are tropospheric liquid and dry precipitations, carbonate substrate components, and products of biological activities of the bird colonies.

The detailed characterization of oceanic insular soils has been a special concern in a number of our works (Dobrovolsky 1985, 1986). Here we merely wish to emphasize that, despite the vast variety of atoll soils, a common feature in their formation is the combination of two factors: (i) availability of large masses of dead organic matter and (ii) well-drained carbonate rocks. The plant remains become rapidly disintegrated by invertebrates, which is the major reason that the detritus composed of small (less than 1 mm in size) particles of carbonized plant tissues is predominant in the organic soil matter. A size fraction study has shown that the percentage of organic detritus increases with the decreasing particle size, and the organic matter accounts for nearly the total of the mass of particles less than 0.01 mm. The inert part of humus in the upper horizon of the soil profile reaches 90%. In the active part of humus, fulvic acids are predominant over humic acids, but the soluble organic acids are subject to a rapid neutralization by carbonate compounds of the soil, which makes the humus content fall sharply down the soil profile.

In atoll soils, the profile distribution of heavy metals parallels that of humus: the metal concentration decreases markedly from the humus horizon down to the soil-forming bedrock. The stores of heavy metals vary in concordance with the variation in humus stores. Noteworthy is the concentration of strontium, the major trace element of coral limestones, is much lower in the humus horizon than in the soil-forming rocks.

Most of the metals contained in the atoll soils are confined to the organic soil matter, and this plays a decisive role in controlling the migratory metal fluxes from the soil. As has been established, an aqueous solution in equilibrium with the humic soil horizon receives metals in rather small amounts, for

example, iron and zinc, some micrograms per gram; copper, tenth fractions of a microgram; and lead, hundredth fractions. Of these, truly soluble forms susceptible to dialysis account for about 50%, with minor variations for different metals. The electrodialysis measurements have shown that the truly soluble forms include, along with cations, also negatively charged species and electroneutral (presumably, organic) molecules. Most of truly soluble forms of iron and zinc are represented by electroneutral particles. Among the soluble forms of copper, about 50% were shown to be cations. Based on the proportion of migratory forms, one may presume that only a very small percentage of metals bound with the soil organics can be absorbed by plants. Apparently, most metals taken up by the atoll vegetation are soluble forms supplied in rainfall.

13 Anthropogenic Deformation of Natural Biogeochemical Cycles

13.1. Human Society as a Factor in the Transformation of the Biosphere

During the last millenia, the natural biogeochemical mass-exchange cycles have been experiencing the ever-increasing influence of economic activities of human society.

The emergence of the first ethnoses and the early civilizations heralded the onset of structural and dynamic alterations of the living matter on the territories colonized by man. Nomadic civilizations, although extending over large territories, were rather slow and favorable in their effects on the natural biogeochemical systems. The impact of agricultural civilizations confined to a limited territory (for example, the Nile valley, or Mesopotamia, an ancient country between the Tigris and Euphrates rivers) was, by contrast, more drastic and brought about a complete change of the natural environment. The more so, if one takes into account the so-called unpredictable consequences of human activities such as the degradation of natural pastures, "man-made deserts," forest fires and many others, one will clearly perceive that the human society, since the very time of its emergence, has become a very important factor in the evolution of the biosphere.

The early activities of man were mainly directed at the living matter of the land and at the biolatent system of the soil. In pursuit of their needs, the humans cut and burned forests, ploughed up steppes, and replaced the natural vegetation by agricultural crops, which could not leave unaffected the biogeochemical structure of terrestrial ecosystems.

Starting from the 19th century, the productive activities have undergone profound changes currently referred to as the industrial revolution. Industry received a potent impetus to its development. The commercial production required at an ever-increasing rate of large masses of minerals that had to be extracted from the Earth's interior. Currently, the annual world production of mineral resources amount to more than $100 \cdot 10^9$ tons, including building materials, ballast for motor roads, and so forth. With reference to the total of the World's land area, this gives about 700 tons of extracted materials for 1 sq. kilometer

of land. However, the human activities embrace not only the outer layer of the Earth's crust, but also the natural waters and the atmosphere. Industrial and domestic needs is about $4.0 \cdot 10^3$ km^3 of water per year, that is, about 10% of river run-off by volume. Molecular nitrogen is extracted from the atmosphere to be converted into reactive forms.

Simultaneously, hundreds of million tons of gases and dust are emitted by industrial plants into the environment, and tens of million tons of domestic, industrial, and agricultural wastes are discharged into surface waters.

The above examples show that the productive activity of human society is a powerful geochemical factor affecting the migration of enormous masses of chemical elements. The human activities exert effect on both the global biogeochemical cycles and local biogeochemical cycles confined to a small territory.

In the mid-20th century, certain chemical elements essential for industrial production are used in amounts comparable to the masses of these elements involved in global biogeochemical cycles. The distinctive feature of most modern industrial technologies is a low economic efficiency which is primarily seen in huge amounts of wastes. These wastes are seldom utilized in allied industries and are either sent to landfills, or released into the environment. The rate at which the contaminating wastes are being accumulated poses a real danger for living organisms, man included.

The hazard of environmental pollution has become, starting from the second half of the 20th century, a major concern of broad sections of the world's people. A vast scope of diverse opinions — scientifically based, fantastic, and purely speculative — have been voiced on this subject. Viewed from a biogeochemical standpoint, any variant to a solution of this problem must take its stand in a thorough study of the effects by technogenic masses on biogeochemical cycles of different rank involved in the overall system of the biosphere. Potentially, the technogenic action can impair the function of global mass-exchange cycles and alter the direction of separate migratory fluxes of elements, which undoubtedly spells disaster for the planetary mechanism providing for the existence of the biosphere. In order to be able to prevent such unwelcome outcomes, one must know which cycles and which ecogeosystems are the most susceptible to this danger.

13.2. Global and Regional Biogeochemical Problems

Depending on the specificity of a mass-exchange cycle, the contaminating component can spread either over the entire biosphere, or over more or less vast territory, or can produce a local effect. One of the problems of

global importance is the putative increase of carbon dioxide in the atmosphere arising from industrial production.

There are ample grounds for this concern. The invention of the steam engine has claimed a wide use of fossil coal as a fuel; the advent of internal combustion engines has necessitated the utilization of petroleum and its products. The commercial combustion of coal proceeded at a vertiginous tempo. In the early 19th century, the world production of coal was about $30 \cdot 10^6$ tons per year; in 1890, it was $700 \cdot 10^6$ tons; in 1913, $1340 \cdot 10^6$ tons; in 1951, $1918 \cdot 10^6$ tons; by 1970, the annual coal production was higher than $3 \cdot 10^9$ tons. The exploitation of oil started in 1856. The world production of oil in 1900 was less than $30 \cdot 10^6$ tons; at present, it has risen to $2 \cdot 10^9$ tons per year. Added to this was the exploitation of natural gas deposits, which also was effected at a very high rate. In 1937, the world production of natural gas was $74 \cdot 10^9$ m^3; it has taken only 30 years to increase tenfold. It is seen, therefore, that the use of natural carbon compounds occurs on a scale comparable to a large natural process. The fossil fuel of any kind converts, when burnt down, to carbon dioxide. A question arises: what can be the further fate of this end product?

According to the available evidence (Bolin *et al.* 1979) the atmospheric concentration of CO_2 until 1850 was about $290 \cdot 10^{-4}$% by volume; a hundred years later, it was $313 \cdot 10^{-4}$%, and in 1978, $330 \cdot 10^{-4}$%. Presumably, during the period until 1978, about $140 \cdot 10^9$ tons of carbon as a CO_2 component has been emitted into the atmosphere through combustion of fossil fuels. Observations of the atmospheric CO_2 concentration have shown that its annual increase during the last years was $2.2 \cdot 10^9$ tons. The global carbon cycle has been discussed in Section 5.2. At present, the overall supply to the atmosphere of carbon as a CO_2 component from industrial sources is estimated to be $5 \cdot 10^9$ tons per year. This amount is about 15 times less than the carbon assimilated by the photosynthesis of the World's land vegetation.

Forest fires, the combustion of firewood and the like supply an additional $4.8 \cdot 10^9$ tons per year, half of this mass being recaptured by the vegetation. Bolin and other researchers are of the opinion that the atmospheric content of CO_2 will annually increase by about a half of the amount of CO_2 as produced by the combustion of fossil fuel. If the fossil fuel consumption retains its annual increase of 4%, the concentration of CO_2 in the atmosphere will reach $380 \cdot 10^{-4}$% at the turn of the 21st century.

The concentrational rise of CO_2 does not in itself spell a great danger, but the increased atmospheric concentration of CO_2 molecules may cause an elevation of air temperature owing to the "greenhouse effect," as has been noted in Section 3.1. This rise in temperature can entail catastrophic consequences indeed.

The meteorologists believe that at present the temperature of the tropospheric surface layer is 0.4 °C higher than was in the 1950-1980s. The prognosis predicts a further increase in temperature by 1.3 °C in 2000, and by 3-4 °C

in 2050. The climatic warming-up proceeding at such a rate will inevitably affect the biosphere as a whole, and its possible consequence will be a nearly 0.5 meter rise of the World's ocean level because of the melting of $30 \cdot 10^6$ km^3 of glacial ice and about the same volume of oceanic ice. The flooding of densely populated coastal territories will entail dramatic situations in the structure and management of the world economy. Thus the theoretical problem of an imbalanced global carbon cycle poses an apocalyptic challenge to economic, social and, consequently, political institutions of humanity.

Attesting to the gravity of the problem is the fact that the Meteorological World Organization (MWO) together with the leadership of the United Nations Environment Program (UNEP) held, starting from 1976, a number of international conferences concerned with this issue. The international scientific community lends a strong support to the view that the reduction of CO_2 emission into the atmosphere is an important world-wide task. At the Toronto conference in 1988, a proposal was submitted to provide measures for a 20% reduction of CO_2 discharge by 2005; at the Hamburg Conference (1989), it was argued that the required reduction should be 30%. In 1988, the MWO and UNEP have instituted a specialized intergovernmental council on this problem, with a representation of more than 40 states.

A point to be noted is that the concerns about the climatic consequences of the elevated CO_2 concentration in the atmosphere have somewhat obscured another, in our opinion no less important, problem. The combustion of enormous masses of coal, petroleum, and gas requires the consumption of still larger masses of oxygen. As has been established (see Sections 5.2 and 5.3), the reserve of free oxygen in the atmosphere was possible only owing to the burial of organic carbon, including the carbon which makes part of fossil coal and natural gas. The ever-increasing combustion of fossil fuel results in the binding of huge amounts of oxygen into CO_2. The world consumption of $5 \cdot 10^9$ tons of carbon as a fossil fuel component requires more than $13 \cdot 10^9$ tons of oxygen.

Now, let us compare the latter value with the mass of oxygen about $230 \cdot 10^9$ tons involved in the biological World's land cycle. The comparison may give the impression that the amount of oxygen consumed in the combustion of fossil fuel is quite insignificant against the total of oxygen produced by the land vegetation. It should be kept in mind, however, that most of the oxygen supplied by photosynthesis must be spent on the degradation of died-off plant organs (sheddings). According to the estimates of Dobrodeyev *et al.* (1976), the preserved (not decomposed to CO_2) dead organic matter saves annually about $1.55 \cdot 10^9$ tons of atmospheric oxygen. This mass is ten times less than the quantity of oxygen annually consumed in the combustion of fossil fuel.

Besides, oxygen is consumed in the oxidation of metals, mostly iron, in the metallurgy industry. The data below can give an idea about the consumption of oxygen in the melting processes. The annual world production of steel is

about 700-800·10^6 tons. The oxidation of 10% of this amount of metal will require about 340·10=6 tons of oxygen. Finally, oxygen is also spent on the oxidation of telluric gases continuously emanated from the Earth's interior. The quantity of oxygen consumed in these processes has never been reliably estimated. We wish to note, by way of conclusion, that the biosphere *in toto* stands up as yet to the oxidation of the products of human industrial activities; however, the caveat must not be neglected that the use of oxygen has reached the level necessitating a close monitoring of the global biogeochemical oxygen cycle.

Industrial wastes and exhaust gases contribute significantly to the imbalance of natural mass-exchange cycles embracing the ecogeosystems of large regions. More than 95% of technogenic sulfur emission is represented by SO_2. Chemically, sulfur dioxide is quite a reactive species. The bulk of emitted SO_2 is derived from the combustion of coals, containing iron sulfides, and of oil commonly high enough in sulfurous organic compounds. Substantial amounts of SO_2 are delivered into the atmosphere during metal production. In 1986, the reported atmospheric emissions (10^6 ton/year) were in USA: CO_2, 18.4; SO_2, 20.3; in USSR: CO_2, 15.4; SO_2, 18.8. In Eastern Europe, the SO_2 emission (10^6 ton/year) was: in 1980, 27.8; in 1985, 26.9; in 1990, 24.3 (Rovinsky 1988). The technogenic emission of sulfur as of 1990 has been estimated to be 100-110·10^6 ton/year.

Sulfur oxides, precipitated in rainfall, afflict the vegetation, destroy the edaphic biota, and cause diseases in the population. Coniferous forests in mountain slopes, brown-red because of sulfuric acid rains, are a dismal sight of the diseased nature in certain countries of Central and Eastern Europe.

The transport of SO_2-laden air masses, heedless of the national frontiers, brings additional socio-political complications into the ecological problem of sulfuric acid rains. There have been reported damages to the territory of the Fennoscandian countries caused by "acid rains" carried over from the industrial regions of Germany.

The agricultural production is a factor strongly affecting the natural biogeochemical cycle of certain chemical elements. The overall area of cultivated soils is at present about 15·10^6 km^2, which makes up 10% of the World's land. The utilization of land for agricultural needs is strongly dependent on both bioclimatic and continental conditions. The available data on the agricultural use of continental soils give the following picture (in % of continental area):

Europe (USSR excluded)	30.8
Asia (USSR excluded)	20.2
North and South Americas	3.5
Africa	14.4
Australia and Oceania	4.1
USSR (% of territory)	9.7

The biological cycle in agricultural territories undergoes a drastic transformation. The native vegetation persisting under natural conditions in a biogeochemical equilibrium with the environment becomes replaced by agricultural crops which are capable of existence in a given ecosystem only under artificial conditions maintained by man.

The vegetation products are not completely returned into the soil, and part of them are removed as harvest. Significant amounts of nitrogen, potassium, and phosphorus and, frequently, of water are artificially enforced into the biological cycling system. Simultaneously, the mechanical disturbance of the soil activates erosive processes and the carry-over of chemical elements beyond the confines of cultivated areas.

According to the data of Kovda (1973), the world harvest of cereals of $1.2 \cdot 10^9$ tons per year entails the involvement in the biological cycle of $48 \cdot 10^6$ tons of nitrogen, $36 \cdot 10^6$ tons of potassium, and $12 \cdot 10^6$ tons of P_2O_5. If one takes into account other agricultural crops, these values will be still higher. The consumption of nitrogen in the world harvest of 1970-1971 was $10^6 \cdot 10^6$ tons; in 2000, the nitrogen consumption is anticipated to be higher than $200 \cdot 10^6$ tons.

The data of Evdokimova *et al.* (1976) for the forest zone of the European part of the USSR with the area of $2.46 \cdot 10^6$ km^2 provide a good demonstration of the biological cycle alterations in a large territory.

In the prehistorical times, the whole of this territory was covered with forests; at present, the forested area has shrunk to $1.5 \cdot 10^6$ km^2; the arable land takes $0.3 \cdot 10^6$ km^2; meadows and pastures, $0.38 \cdot 10^6$ km^2; towns, villages, transport lines, rivers and lakes, $0.24 \cdot 10^6$ km^2. All those changes have resulted in a sharp reduction of the phytomass and associated therewith chemical elements. The agricultural crops, amply manured with fertilizers, entrain large amounts of nitrogen, phosphorus, and potassium in the biological migration, much in excess of those by the natural forest vegetation. However, a significant part of elements are removed by man: $11 \cdot 10^6$ tons of nitrogen, $1.1 \cdot 10^6$ tons of phosphorus, $4.5 \cdot 10^6$ tons of potassium, and $5.3 \cdot 10^6$ tons of calcium as components of harvested crops and timber are annually delivered from the entire territory. The stream loss of calcium from the territory is significantly higher than the supply of this element in mineral manuring and soil liming. Summarized in Table 13.1 are comparative data for the migration of chemical elements in the territory of the European part of the USSR prior to human activities and at the present time.

The data in Table 13.1 show that the annual turnover of chemical elements has suffered a larger change in the steppe zone where the agricultural activity was more intense. Of the formerly intact territory of about $0.3 \cdot 10^6$ km^2 of the southern steppes grown with grass vegetation, $0.22 \cdot 10^6$ km^2 has been plowed up. The changes recorded here are quite specific. Despite the considerable

Table 13.1. Anthropogenic Transformation of Elemental Mass Exchange in the Forest and Steppe Zones of the European Part of the USSR (according to the data of Evdokimova *et al*. 1976)

Zone and involvement	Elements and annual turnover per total zone area (10^6 ton/year)									
	Nitrogen		Phosphorus		Potassium		Calcium		Sulfur	
	(*)	(**)	(*)	(**)	(*)	(**)	(*)	(**)	(*)	(**)
Forest zone ($2.42 \cdot 10^6$ km^2)										
Supplied in precipitation	0.87	0.87	0.03	0.03	1.09	1.09	1.52	1.52	2.61	2.61
Involved in biological cycle	21.1	20.6	1.9	2.38	5.5	9.91	9.2	8.1	1.5	1.46
Supplied in fertilizers	0.0	0.60	0.0	0.18	0.0	0.45	0.0	12.0	0.0	0.30
Lost in harvested crops and deforestation	0.0	11.3	0.0	1.11	0.0	4.54	0.0	5.31	0.0	0.60
Lost in run-off	0.8	1.21	0.17	0.17	2.0	6.06	7.3	16.6	5.4	4.6
Steppe zone ($0.31 \cdot 10^6$ km^2)										
Supplied in precipitation	0.124	0.124	—	—	0.123	0.124	0.93	0.93	0.46	0.68
Involved in biological cycle	6.5	2.01	0.25	0.34	0.7	0.8	5.5	0.73	0.5	0.095
Supplied in fertilizers	0.0	0.75	0.0	0.25	0.0	0.38	0.0	—	0.0	—
Lost in harvested crops	0.0	1.4	0.0	0.2	0.0	0.64	0.0	0.47	0.0	0.08
Lost in run-off	—	0.3	—	0.1	—	2.0	—	1.5	—	0.30

Note: (*) intact by human activities; (**) at present.

Table 13.2. Industrial Production and Natural Migration of Nitrogen, Phosphorus, and Potassium in the World's Land

Process	Elements and migration rate (10^6 ton/year)		
	Nitrogen	Phosphorus	Potassium
Industrial (N) or mining (P and K) production	60*	40	16
Natural stream loss			
in solution	18	0.8	61
in suspension	6	20	283
Natural supply in precipitation	50	(nil)	65
Content in products of natural vegetation	3500	350	1800

*Exclusive of industrial and domestic wastes amounting to about $40 \cdot 10^6$ tons of N per year

amount of nitrogen applied in fertilizers, the uptake of nitrogen has decreased in comparison with the intact steppes. The turnover for both phosphorus and potassium does not appear to be much altered; however, the aqueous migration of elements has grown markedly because of soil erosion. This is especially true of potassium whose stream loss is several times higher than the intake of this element in fertilizers.

The Earth's population grows progressively, which makes its provision with food products one of the most urgent tasks. The implementation of this task requires an ever-increasing application of fertilizers, which, in turn, necessitates the updating of old and the building of new mining works, of new integrated chemical plants for processing of raw minerals into fertilizers. At present, the artificial involvement of larger masses of chemical elements in the biological cycle is a major means to increase the crop yield.

The data presented in Table 13.2 allow us to compare the commercial production and migratory masses for nitrogen, phosphorus, and potassium. As is seen, the amounts of nitrogen and phosphorus, artificially directed into the biological cycle, are in excess of the amounts of these elements naturally involved in the aqueous migration.

The mass distribution for nitrogen in the world's agricultural production merits a special comment. The pertinent data are summarized in Table 13.3. One will observe, in comparing the data in Tables 13.2 and 13.3 that in 1970,

Table 13.3. Distribution of Nitrogen in Agricultural World Production (Biological Cycling in Nature ... 1980)

Item	Turnover index (10^6 ton/year)	
	1970-1971	2000 (predicted)
Loss in harvested crops	106	212
Application in fertilizers:		
total	50	165
mineral	32	120
organic	27	45

about $30 \cdot 10^9$ tons of fertilizer nitrogen per year was applied to the cultivated soils of the World Land; in 1990, it was about $60 \cdot 10^9$ tons, with an anticipated increase to $120 \cdot 10^9$ tons per year in 2000. In view of the agrochemical intensification of agriculture, there arises a problem of nitrogen with a bearing not only on the biogeochemical, but also on the ecological issues.

First, the artificial introduction of large amounts of nitrogen into the cultured soils impairs the mass-exchange balance within the soil-vegetation system. The excess nitrogen not included in the biological cycle is actively involved in aqueous migration. Nitrogen compounds become accumulated in geochemically subordinate ecogeosystems such as negative relief elements, lakes, and hydroelectric station reservoirs. This stimulates an increased growth or even overgrowth of aquatic vegetation and leads to an overload of water bodies with dead plant remains and decay products.

Second, an abnormally high content of soluble nitrogen compounds in the soil entails their elevated concentrations in agricultural food products and drinking water. As has been established, nitrites, on their intake by the organism, are capable of forming compounds that impair the oxygen metabolism in the human blood, with the resulting development of a pathologic state, the methemoglobinemia. This state is accompanied by grave complications, especially in children.

The available data have allowed us to reach a conclusion that, owing to the high openness of natural mass-exchange cycles linking separate ecogeosystems, the normal performance of the global nitrogen cycle is retained. However, in certain agricultural regions the excess nitrogen masses may fail to enter into the biological cycle, become entrained in the aqueous migration and impair therefore the normal performance of biogeochemically subordinate ecogeosystems.

13.3. Local Anthropogenic Biogeochemical Anomalies of Heavy Metals

Among numerous consequences of human productive activities of special concern is the progressive accumulation of metals in the environment. Different metals — those used since the ancient times and those that have gained acceptance recently — are being applied in industry at an ever-increasing rate. This trend is easily perceived in Fig. 27 showing the mining rate for copper ore (worked out already in ancient times) and for molybdenum and uranium ores whose industrial processing started only in the 20th century.

At present, the world production of metals is characterized as shown below (in ton/year):

$n \cdot 10^8$: iron;
$n \cdot 10^7$: manganese, aluminum;
$n \cdot 10^6$: copper, zinc, lead;
$n \cdot 10^5$: nickel, tin;
$n \cdot 10^4$: molybdenum, uranium, tungsten, cobalt, cadmium, vanadium;
$n \cdot 10^3$: mercury, silver.

These estimates provide evidence that the metals are extracted in amounts not proportional to their abundances in the Earth's crust and pedosphere which modulated the development of terrestrial forms of life. For example, the crustal abundance for aluminum is thousands of times higher than that for copper, whereas the modern productions of these metals are quite close differing merely several folds. The crustal abundance for molybdenum is nearly a hundred times smaller than that for vanadium, whereas the commercial production of molybdenum is much higher.

The most essential, at first sight even paradoxical, feature of the world-wide utilization of metals is their active dispersal. The routes of technogenic dispersal of metals are quite diversified: a major one is the emission into the atmosphere during the metallurgic processing of ores. A significant part of metals are already lost at earlier stages — in transportation, beneficiation, and separation. As noted by Beus and coworkers (1976), the world-wide dispersal of commercial metals within a decade of 1965-1975 was (in thousand tons): copper, 600; zinc, 500; lead, 300; molybdenum, 50.

The modern metal-working technology is highly noneconomic — to an extent that may instill to a rationalist the heretic suspicion that the thoughtless squander of metals is being done intentionally. Enormous masses of metals are used in chemical, paper, electrotechnical and other branches of industry to be finally lost into wastes. The metals are *en masse* detritted, abrased, and dispersed during

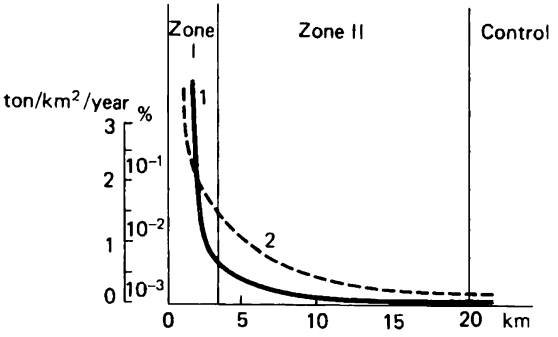

Fig. 27. Areal mass distribution of precipitated contaminating metals within a biogeochemical impact anomaly. One will observe the sharp decrease of metal fall-out concentration outside the I zone

the operation of various machines and mechanisms. A significant part of certain metals and trace elements are produced with the seemingly sole objective to disperse them over the Earth's surface. By way of example, one may refer to the production of alkylated leads as additives to motor fuel, also the use of mercury and arsenic for the fabrication of agricultural pesticides.

Apart from the branches of industry that produce or utilize metals, there are other contributors to the technogenic dispersal of metals, especially those specialized in the combustion of fossil fuel, chiefly coal.

The masses of heavy metals, annually supplied to the environment owing to the productive activity of man, are at present comparable with the amount of metals involved in the global biological cycles; demonstrative of this are the data presented in Table 13.4.

The amounts of manganese and chromium annually delivered to the biosphere from the coal combustion are close to the stream loss of their soluble forms in the world rivers. The annual production of copper, lead, tin, and cadmium is much in excess of both the stream loss of their soluble forms and the annual uptake by vegetation.

If the masses of metals, emitted into the air, could spread, like gases, over a large space to be washed out of the troposphere in rain- and snowfall, then their supply to the World's land surface, or even to the land surface of the Northern Hemisphere would not exceed the natural limits to which the vegetable and animal organisms are tolerant. Unfortunately, the bulk of metal wastes is confined within a close vicinity of the pollution source. As a consequence, the living organisms of local habitation suffer a severe environmental impact, with the emergence of biogeochemical anomalies around the industrial contaminator.

Table 13.4. Involvement of Heavy Metals in Technogenic and Natural Migration

Element	Annual output	Release by coal combustion (data as of 1980)	Annual growth uptake by land vegetation	Stream loss of soluble forms
Mn	8500	430	410400	440
Cu	6000	30	1376	287
Zn	4400	140	5160	820
Pb	2400	27	215	44
Cr	2000	49	309	41
Ni	560	14	344	123
Sn	180	3	43	21
Mo	73	6	86	37
Co	26	5	86	10
Cd	26	2	8.5	8.2

Note: All values are in 10^3 ton/year.

It is to be recalled that heavy metals are very essential components of biocatalysts and bioregulators for important physiological processes. For this reason, a high concentrational rise of heavy metals in a finely-dispersed and, consequently, highly-active state in the environmental medium produces a strong effect on the living organisms. In the 1st Program on the global environmental monitoring system (Munn 1973), only three metals — mercury, lead, and cadmium — were named in a list of 12 of the most hazardous contaminants. However, in 1980, the Executive Director for the United Nation Environmental Program (UNEP) noted emphatically in his report that the hazard of contamination with heavy metals took the second lead after the CO_2 problem on global climatic changes. Seven more candidates among the metal contaminants: manganese, tin, copper, molybdenum, chromium, nickel, and cobalt, were added to the previously mentioned three. All these facts furnish evidence for the growing concern about potentially detrimental effects that the technogenically supplied metals and elements can exert on living organisms and their communities.

Two zones are commonly distinguished within the confines of a technogenic biogeochemical anomaly (Fig. 27). The first zone, immediately adjacent to the source of contamination, is characterized by a severe injury of the natural ecogeosystem. Frequently, this zone is destitute of vegetation, its biolatent soil system is completely degraded, and the edaphic animals and microorganisms

are to a large extent destroyed. In the second, more extensive zone, one will observe the suppression, rarely the disappearance of certain components of the biota. At the periphery of this zone, the natural ecogeosystem appears outwardly unchanged, although its components (soil, plants) exhibit elevated concentrations of contaminant elements, which may potentially affect the succeeding generations.

The zone of severe contamination around the Sudbury copper-nickel plant (Canada) has a radius of 3 to 5 km. The second zone extends as far as 20 km. Within the first zone, the biota and soil have been practically destroyed, the surficial fall-out of copper and nickel has been hundreds and even thousands of times greater vis-à-vis the global background. The concentration of nickel in the soil in a radial direction from the source falls off rapidly as a power law. Within the second zone, the concentrational decrease is linear down to the level of local geochemical background. In this zone, only certain of the vegetable and animal species are inhibited.

An analogous situation has arisen in the vicinity of the large Norilsk metallurgical plant (northern Siberia) and in the Kola Peninsula (USSR), where two copper-nickel plants are situated. Around these, vast biogeochemical anomalies have emerged, with the nickel and copper concentrations at the central region more than 100 times higher than the background level (Survey of the Background State ... 1988). One of those anomalies extends as far as the northern part of Norway and Finland (Fig. 28).

In the steppe landscapes, technogenic geochemical anomalies are more extensive; nonferrous metallurgy plants are found at the epicenter of dispersion halos of lead, zinc, copper, and arsenic with a radius of 5 to 20 km. Around a large lead-refining plant in the dry steppe zone of South Kazakhstan (USSR), the halo of technogenic dispersion spreads out as far as 25-30 km. The concentration of the contaminant metal (be it a major component or an admixture to the ore) decreases as a power law from the source down to the background level (see Fig. 29).

The concentration of technogenically dispersed elements in the snow cover is much smaller than in the soil. Around the Tikkurila lead smelter in the vicinity of Helsinki (Finland), a zone of heavy soil contamination extends to a radius of about 500 m, with the lead concentration 24 times higher than the local geochemical background ($378 \cdot 10^{-4}$ % in the plowing horizon). At a distance of 2 km, the metal concentration decreases remaining, however, several-fold higher than that of background. In a four-month-old snow cover, the lead concentration falls off rapidly: at a distance of 100-200 m from the smelter, it is 10-47 kg/ha; at a distance of 1 km, 1.1-1.3 kg/ha; at a distance of 2.5-3.5 km, 0.3-0.2 kg/ha (Toikka, 1980).

The size of anomalies is dependent, apart from the output of the smelter, on a variety of other factors such as the period of productive performance,

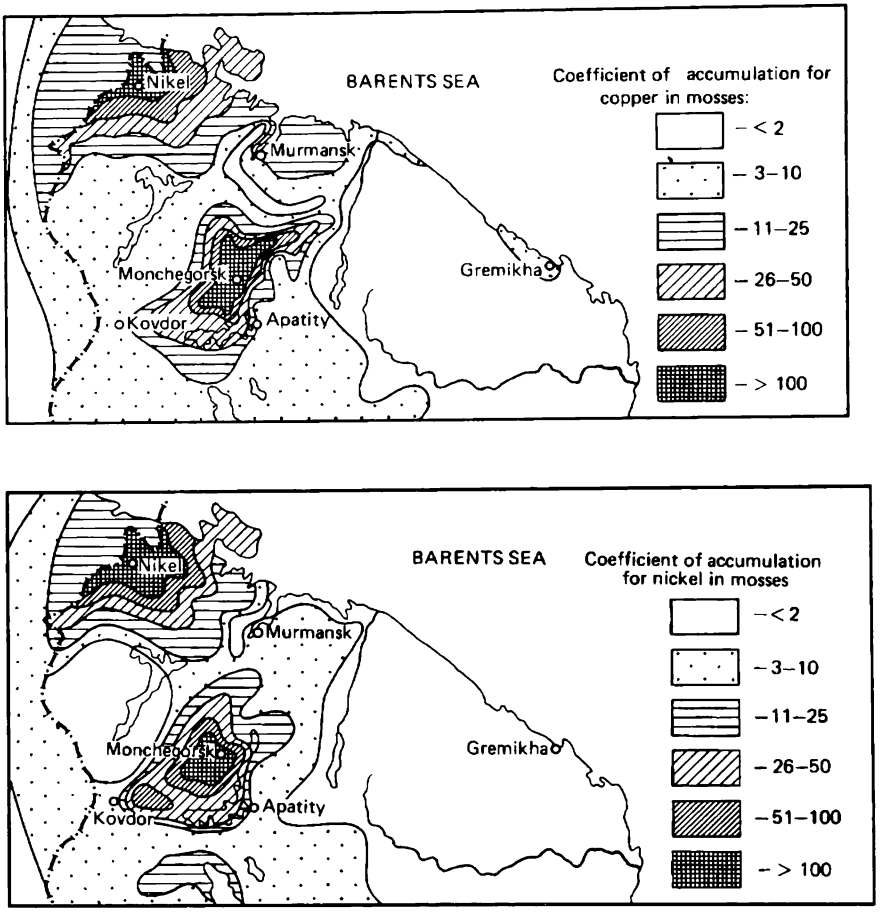

Fig. 28. The vegetation cover areas in the Kola Penisula polluted with copper (top picture) and nickel (bottom picture)
(According to the Survey of the Natural Environmental Background USSR, 1988)

technology, and so forth. The altitude at which the wastes are emitted into the atmosphere also plays a role. Commonly, it may be accepted that, with a high chimney stack, a significant concentration of contaminants arises in the surficial atmospheric layer at a distance of 10-14H from the source, where H is the height of the chimney stack. With chimney stacks 10-15 m high, a maximum of contaminant concentration in the air is recorded in an immediate vicinity of the source.

The concentrational proportions of technogenically dispersed metals in the air, rainfall, vegetation, and soil escape an easy estimation. Around a lead smeltery in the Primorski Territory of the Far East (USSR) under the condition of a temperate monsoon climate with an annual 1000 mm rainfall, the zone of maximum metal concentrations in the air extends as far as 2 km from the source (Geochemistry of Hypergenesis Zone 1976). In this zone, the metal concentration in the surficial atmospheric layer is 100-1000 times higher than the local geochemical background; in the snow cover, this is 500-1000 times less. The second zone extends from 2 to 4 km, with its aerial metal concentration about 10 times smaller than that of the first zone. One might have suggested a third zone of 4 to 10 km where sample types exhibited occasionally an elevated metal concentration.

The first and second zones of polluted surficial air are zones of destroyed natural ecogeosystem and inhibited vegetation. The area of metal dispersal in the snow cover is smaller than in the atmosphere; analyses of tree leaves for metal content have shown that the area of elevated fall-out metal concentration was roughly within the confines of high aerial metal concentration. The snow analysis has shown that the seasonal supply of precipitated metals (in g/km^2) was: copper, 2.4; zinc, 5.5; lead, 615; cadmium, 16.6; arsenic, 18.8. In the second zone, the results were: lead, 26; zinc, 3; and arsenic, 1.2.

It is noteworthy, that the proportions of different forms of dispersed elements vary with distance from the pollution source. In the first zone, water-soluble forms account for a mere 5-10%, and the bulk of precipitated material was formed by dust particles of sulfides and oxides. At a distance of 1.5 km from the smelter, the relative content of water-soluble forms of lead was 55%, and at a distance of 4-5 km, 80-90%. It is to be inferred therefore that a greater part of solid dust particles are deposited near the source of contamination, whereas the water-soluble forms are carried over to longer distances and are washed out of the atmosphere in rainfall.

In theory, the biogeochemical anomalies of technogenic origin are envisaged as a set of concentric circumferences whose radii scale the decreasing concentration of a contaminating metal in plants and in the soil in a radial direction from the center (source of contamination) towards the periphery. In reality, owing to the prevailing winds, relief features, vegetation, and rainfall regime, the zone pattern is subject to variation. By virtue of this, the biogeochemical anomalies of heavy metals are most commonly shaped into elongate or irregular contours.

The configuration of soil anomalies is further complicated by the technogenic supply of metals, with the resulting change in the natural metal proportion of the mineral soil substrate.

As an example, we shall refer to the geochemical heavy-metal anomalies in the eastern seashore of the Spencer Bay (South Australia). The territory of

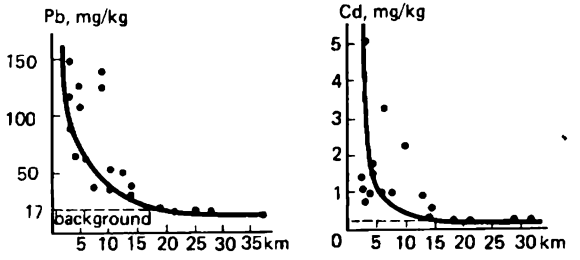

Fig. 29. The concentration dropp-off of the major metal contaminant (lead) and major contaminant (cadmium) in the soil within the confines of a biogeochemical impact anomaly at a different distances from the pollution source (leadsmeltery) (Zyrin *et al.* 1980)

interest expands to a coastal plain and a residual denudation plateau elevated to 600 m above the sea level. The coastal plain is composed of recent deposits, and the plateau, of proterozoic crystalline rocks. The plateau, shaped into a ridge in the meridional direction, lowers a barrier to the atmospheric precipitation from the sea. This results in the annual rainfall of 500-600 mm in the plateau as compared to a mere 300-400 mm in the coastal plain.

In the bay area, the only source of industrial contamination is a smelter in Port Pirie, in exploitation since 1889.

The Australian geochemists (Cartwright *et al.* 1977) have analyzed the soil cover for metal content and found two distinct geochemical anomalies. One of these is around the smelter, the other is confined to the residual plateau. The technogenic origin of the lead anomalies is beyond a shadow of doubt. In the rocks, constitutive of the plain and the plateau, the metal concentration is not higher over $25 \cdot 10^{-4}$%, whereas within the confines of the anomalies, it is in excess of $50 \cdot 10^{-4}$% (see Fig. 30). The anomaly around the smeltery has been produced by the atmospheric fall-out of the products emitted from the chimney stacks; it extends in the south-southeast direction owing to the prevailing winds. The lead anomaly in the residual plateau appears to have originated in the atmospheric precipitation which supplied a large part of water-soluble lead forms in rainfall.

The zinc emissions have yielded a more complicated distribution pattern (Fig. 30, B). The elevated zinc concentration in the soil around the smeltery is, like that of lead, of technogenic origin. The less distinct zinc anomaly in the plateau might have arisen from a different source. In the crystalline slates of which the plateau is composed, the zinc content ranges from 63 to $160 \cdot 10^{-4}$%. In

the plain soils overlying the recent deposits, the zinc concentration is $16 \cdot 10^{-4}$%. Cosequently, the anomaly, confined within a $20 \cdot 10^{-4}$% isoline, may in equal measure be attributed to a technogenic pollution and to a high natural concentration of zinc in the bedrock.

The dispersal of metals is effected not only by metallurgy and metal-working plants; plants of other industries also contribute to the environmental metal contamination. The raw material for fabrication of phosphorus fertilizers contains admixed copper, zinc, lead, uranium, and other elements which are scattered around the producer plant. The production of paper is accompanied by a dispersal of mercury. Heavy-duty thermal power stations create halos of dispersion of sulfur oxides and heavy metals 10-20 km across. Any town, however small it may be, is a source of environmental metal contamination. The environmental impact of a small town is reflected in a higher content of trace elements in the vegetation within a radius of 2-3 km.

Specific biogeochemical lead anomalies arise along the motor roads. Tetraalky lead is added to motor fuel as an antidetonant to increase the efficiency of an internal combustion engine. Lead is emitted in the exhaust gas in the form of finely-dispersed solid particles of oxides, chlorides, fluorides, nitrates, sulfates, and other species. About 20% of the particles are larger than 0.005 mm in size. They precipitate in close vicinity of the motor road. Particles of smaller size containing about 60% of exhausted lead have a longer air-borne residence time and are precipitated within the confines of a relatively wide zone. The remaining 20% is carried away with the wind to a more or less long distance.

The metal concentration in the soil is dependent on the volume of traffic. The highest values recorded in the Western Europe are 600-700 μg/g. The width of the road-side anomalies for lead level in the soil is greatly varied depending on the local conditions; as evidenced by the results of studies carried out in Belgium, Switzerland, Germany, and a number of other countries, it reaches 100 meters.

In the Western European countries, prior to the enactment of the laws on lead dosage in motor fuel, the lead concentration in the motor road-side grass vegetation was 40-50 μg/g. The highest level of contamination was recorded in the vegetation 5-10 m from the road-side, as well as in the vegetation of the dividing strip between traffic lanes. The zone of lower lead concentration extends to 50-100 m from the road-side; however, more extensive anomalies have been recorded. The available evidence has given the conclusion that the width of the zone of anomalous metal concentration in vegetation is subject to a higher variation than that in the soil.

The analysis of outer tree bark in the forest strips along the motor road has shown that the lead concentration reaches its maximum at 1-2 m above the ground level, and then falls off rapidly with height. Thus, the biogeochemical

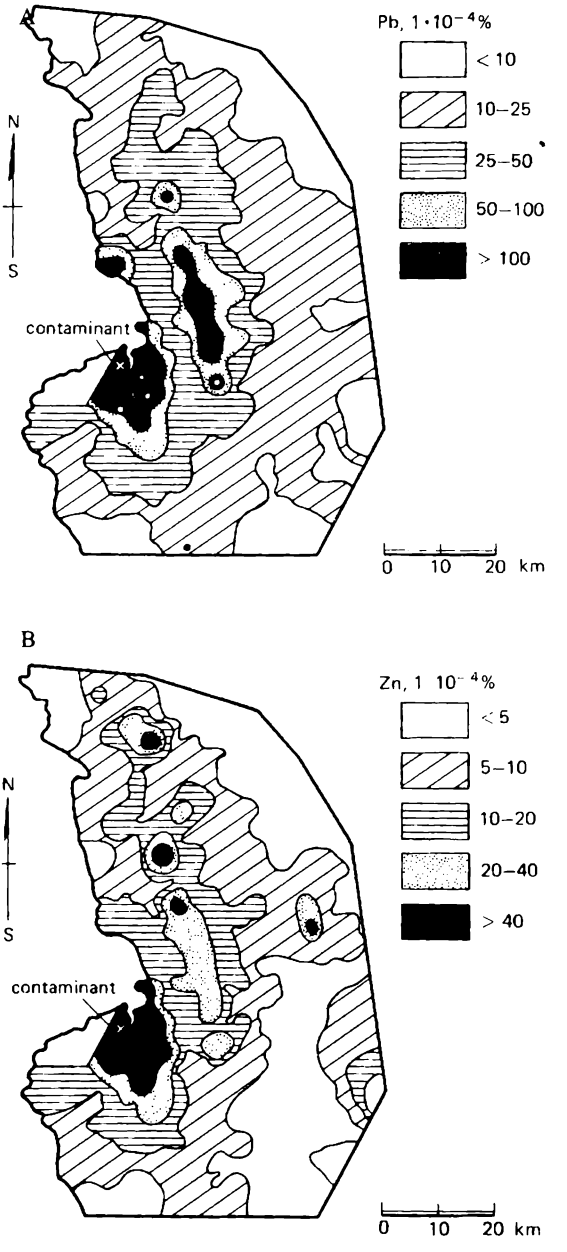

Fig. 30. Technological lead (A) and zinc (B) anomalies in the vicinity of Port Pirie, Australia (Cartwright *et al.*, 1977)

motor-road lead anomaly is restricted to a long corridor 100-200 m in width and not greater than 5-8 m in height.

A characteristic feature of technogenic biogeochemical anomalies is their dynamism and parametric variability. To a large extent, this should be attributed to the fact that the atmospheric migration is a major causative factor in these anomalies. The configuration of a biogeochemical anomaly is influenced by seasonal variations such as the change from a dry period to rainy weather, or the change in prevailing winds.

In particular, the surficial lead concentration in the traffic-polluted soil is not constant and, during the annual period, tends to increase from spring to autumn. A similar tendency is observed in roadside plants during their vegetation period. The concentrational metal growth in the soil and plants appears to be linked to a gradual accumulation of finely-dispersed particles emitted in the exhaust gases. The noted regularity is impaired by rains which wash the lead-containing precipitates off the plants and soil surface. Due to the action of the wind, the lead distribution in plants on both sides of the road is often asymmetric.

A specific biogeochemical situation has arisen in large cities and industrial centers. The urbane atmosphere, saturated with gases and technogenic aerosols, is also strongly polluted with heavy metals, primarily, lead from exhaust gas. A vast variety of chemical elements and compounds are accumulated in industrial and domestic wastes. As has been established, the dust from metal-working plants is high in alloying metals and hard alloys (those of tungsten, molybdenum, chromium); the slime in the sewage-treatment system of electroplating shops accumulates cadmium, bismuth, silver, and tin. The domestic garbage contains many elements in elevated concentrations.

Annually, the refuse sites receive in the wastes from large cities the heavy metals in amounts comparable to the annual production of mining works (Saet *et al.* 1990). The progressively growing waste masses lead to elevated concentrational levels of heavy metals in the vegetation and the soil cover of the circumurbane zone. The application of the composts from domestic garbage to soil manuring in the privately tilled plots can cause abnormally high concentrations of heavy metals and other elements in the harvested vegetables and fruits.

Overall, the modern large cities and industrial urbanized agglomerations represent in fact enormous technogenic geochemical and biogeochemical anomalies. The paradox of the situation resides in the fact that both the absolute and the relative number of urban population grows incessantly, and, simultaneously, the emission of all kinds of waste from the industrial civilization is the most intense precisely in the cities. The geochemically abnormal environment affects detrimentally the health of the population and will lead, almost with certainty, to unpredictable catastrophic consequences for subsequent

generations. The biogeochemistry of big cities must be regarded as one of the top-priority problems facing science at the turn of the second and the third millenia of our era.

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